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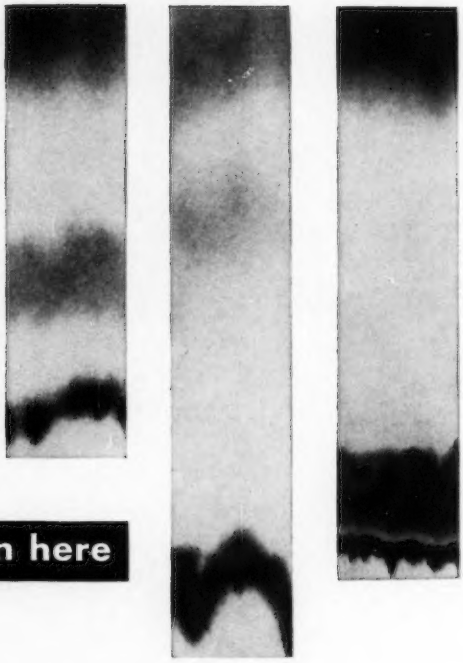

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ANALYTICAL ABSTRACTS

1.—GENERAL ANALYTICAL CHEMISTRY

General reviews of progress, reagents and methods of general application.

1175. **Proceedings of the fifteenth International Congress of Pure and Applied Chemistry (Analytical Chemistry).** Lisbon. 1956. Vol. I.—This is the first of three volumes and contains 111 communications of which 49 were delivered to the section on Microchemical Methods and 62 to that on Electrical Methods. Eighty-four papers have not been published elsewhere. A list of titles and authors follows with references to journals in which the papers have appeared. The language is English unless otherwise stated. **The study and identification of emetine,** M. L. Bastos, 49–55 (in Portuguese). **A new automatic apparatus for the determination of centigram amounts of carbon and hydrogen in organic substances,** B. Bobrański, 56–68 (in German) (*Mikrochim. Acta*, 1956, 1735). **New specific reaction for the identification of khellin,** A. J. Correia Ralha, 69–72 (in Portuguese) (*Rev. Portug. Farmác.*, 1956, **6**, 109). **Micro-analytical methods for the determination of antimony, tin and lead and their application to the analysis of tin-base and lead-base alloys,** C. Cimerman and M. Ariel, 73–84. **Micro-determination of fluorine,** E. Debal, R. Levy and H. Moureau, 85 (in French). **Organic micro-determination of carbon by conductimetry,** R. Delaby, R. Damiens and G. Tsatsas, 86–87 (in French). **Separation and determination of traces of boron in silicon,** L. Ducret and P. Seguin, 88–100 (in French) (*Anal. Chim. Acta*, 1957, **17**, 207). **Causes of error in the Kjeldahl micro-determination of nitrogen by the nesslerisation method,** J. González Carreró, O. Carballido Ramallo and F. Gómez Vigide, 101–112 (in Spanish). **Detection and determination of traces,** G. Gorbach, 113–119 (in German). **The micro-determination of molecular weight of dissolved substances by direct measurement of vapour pressure,** H. Gysel and K. 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Heyndryckx, 184–197 (in French). **Hydroxy derivatives of triphenylmethane as indicators in thoriometry,** R. E. Longo, 198–205 (in Spanish). **The Kjeldahl determination of nitrogen: a critical study,** H. A. McKenzie, R. G. Wake and H. S. Wallace, 206 (summary only). **Concentration of trace elements,** C. Mahr and H. Klamberg, 207–212 (in German). **Selective micro-determination of alkoxy groups by gas - liquid chromatography,** F. Martin and S. Vertalier, 213–228 (in French). **Possibilities of acidimetry and alkalimetry of mercuric salts,** R. Montequi, A. Doadrio and M. F. Santiso, 229–238 (in Spanish). **Direct alkalimetry of potassium tetraphenylboron in the presence of mercuric chloride,** R. Montequi, A. Doadrio and C. Serrano, 239–245 (in Spanish). **Quinones as characterising reagents for cysteine,** E. Neuzil and J. C. Breton, 246 (French summary only). **Identification of flavanonols of some *Rosaceae* and *Leguminosae* by a new colour reaction,** H. 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Green, 288–296 (in French). **A method for the simultaneous micro-determination of C-, H- and N-content of organic compounds with one weighing,** W. Schöniger, 297–299 (in German) (*Mikrochim. Acta*, 1957, 545). **Iodimetric micro-procedure for the determination of phenol in the presence of reducing substances,** E. Schulek and K. Burger, 300 (German summary only). **Analysis of fluorinated organo-metallics. I. Determination of fluorine and silicon in organic fluorosilicon compounds,** O. Schwarzkopf and R. Henlein, 301–311. **Determination of C-CH$_3$ groups,** O. Schwarzkopf and D. D. Phillips, 312–325. **New rapid method of separation and determination of traces of boron. Application to the determination of boron in silicon,** L. Ducret, 326–336 (in French). **Spot tests for cobalt and sulphites based on the induced oxidation of cobalt - azide solutions,** P. Senise, 337–342 (part published in *Mikrochim. Acta*, 1957, 640). **Micro-analytical researches on halogen ions,** Y. Servigne, 343 (French summary only). **A new simple micro-determination of iodine in biological material,** H. Spitzy and M. Rease, 344–352 (in German)

(*Mikrochim. Acta*, 1958, 488). **Method of precipitation of hydrated oxides of ferric iron and manganese at constant pH: applications in micro-analysis,** M. Tanaka, 353–361 (in French). **Gravimetric micro-determination of silver with 1:2:3-benzotriazole,** N. Waldbott von Bassenheim, 362–367 (in Spanish). **Micro-determination of sulphur,** M. Večeřa, 368–381 (in German). **Determination of trace elements in phosphate minerals,** R. Vigier, 382–390. **Trace elements in edible fats. IV. Separation and spectrophotometric determination of zinc,** A. Vioque and M. P. Villagrán, 391–399 (in Spanish) (*Grasas y Aceites*, 1956, **7**, 239). **Microchemical techniques and methods applied to problems in the coal industry,** J. H. Wood, 400–436. **Automatic micro-analytical apparatus for gases in metals,** S. Yanagisawa, M. Seki, Y. Watanabe and S. Nakamura, 437–445. **Detection of traces of iron,** F. Feigl and A. 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Popescu, 513–536 (in French). **Analysis of mixtures of inorganic ions by differential electromigration on a paper disc,** G. Cetini, 537 (Italian summary only). **The study of silver chloride complexes at 25°. II. Study of hydrochloric acid solutions,** H. Chateau and B. Hervier, 538–554 (in French). **Polarographic determination of semicarbazones,** D. M. Coulson, 555–565. **Electrochemical reduction of water and of hydrogen ions,** J. Coupez, 566–571 (in French). **Coulometry of 1 mg of uranium,** J. Coursier, J. Hure and C. Cornet, 572–581 (in French). **The improvement of the measurement of polarographic currents,** D. Cozzi, S. Vivarelli and G. Piccardi, 582–589 (in Italian) (*Z. Electrochem.*, 1957, **61**, 845). **Polarography in liquid ammonia,** R. Curti and S. Locchi, 590–596 (in Italian). **Coulometric determination of mono- and di-hydric phenols,** F. Čůta and Z. Kučera, 597–604 (*Chem. Listy*, 1958, **52**, 595). **Adsorption kinetics and electrode processes,** P. Delahay and I. Trachtenberg, 605–625 (*J. Amer. Chem. Soc.*, 1957, **79**, 2355). **Conductimetric methods for the determination of bismuth,** C. Drăgulescu and D. Lazăr-Jucu, 626–632 (in French). **Use of polarography in the micro-determination of lead in blood,** R. Fabre, R. Truhaut and C. Boudene, 633–638 (in French). **A new rapid method of electrogravimetry at vibratory electrodes,** G. Facsko, 639–653 (in French). **The limits of applicability of the measurement of dielectric constant to organic analysis,** L. Felloni and E. Tantillo, 654–660 (in Italian) (*Ann. Chim., Roma*, 1957, **47**, 751). **Coulometric potentiometric determination of ascorbic acid,** B. Foresti and S. Musumeci, 661–666 (in Italian). **Potentiometric titration of weak acids and bases in dilute aqueous solution,** J. C. Gage, 667–681 (*Analyst*, 1957, **82**, 219). **Classification of titration reactions and end-point determination in potentiometric analysis,** F. L. Hahn, 682–687 (in German). **Potentiometric titrations in non-aqueous solutions. I. An empirical acidity potential scale of twelve solvents,** H. B. van der Heijde and E. A. M. F. Dahmen, 688–709 (*Anal. Chim. Acta*, 1957, **16**, 378); **II. Anomalous behaviour of weak oxygen acids in inert and weakly basic solvents,** H. B. van der Heijde, 710–722 (*Anal. Chim. Acta*, 1957, **16**, 392). **Double complexing agents in polarographic analysis. The use of EDTA - KCN base solution,** M. Ishibashi, 723–733. **High-frequency titration of phenols and carbonyl compounds in non-aqueous media,** K. J. Karrman, G. Johansson and E. Christensson, 734–739. **New method of hydrogen ion activity determination in aqueous and non-aqueous solutions with reversible and irreversible electrodes,** P. Kirkov and M. Djonova, 740–749. **Oxidation - reduction potentials in systems not attaining equilibrium,** J. M. Landucci, 750–754 (in French). **A 250 Mc/sec. high-frequency titrimeter,** E. S. Lane, 755–768 (*Analyst*, 1957, **82**, 406). **Methods of determination of sulphonamides suitable for the control analysis of individual drugs,** C. G. Macarovici, 769–782 (in French) (*Revue de Chimie*, 1956, **1**, 79). **The Ilkovic equation and polarographic current - time curves,** H. A. McKenzie, 783 (summary only). **Measurements of the dissociation constant of picolinic acid,** J. C. Merlin and G. Thomas, 784–790 (in French). **Orthophosphoric acid as a solvent and base electrolyte in direct inorganic polarographic analysis,** G. W. C. Milner and L. J. Slee, 791–812 (*Analyst*, 1957, **82**, 139). **The use of complexing agents in the separation of inorganic ions by differential migration in an electric field,** M. Milone and G. Cetini, 813 (Italian summary only). **Relations between the half-wave potentials and the chemical constitution of nitrogenous compounds,** L. Moelants and R. Jansen, 814–820 (in French) (*Bull. Soc. Chim. Belg.*, 1957, **66**, 209). **Polarographic determination of the oxidation of phenylenediamines in solution. Study of the inhibitory action of sulphite,** L. Moelants, 821–832 (in French). **Study of the nitration and polarographic determination of phenylalanine,** D. Monnier and R. Guerne, 833–838 (in French). **Amperometric titrations of micromolar solutions,** J. G. Nikelly and W. D. Cooke, 839–846 (*Anal. Chem.*, 1956, **28**, 243). **An electronic apparatus for measurements of magnetic susceptibility—applications,** A. Pacault, B. Lemanceau and J. Joussot-Dubien, 847–852 (in French). **Polarographic determination of heavy cations in wines,** J. Bonastre and R. Pointeau, 853–859 (in French) (*Chim. Anal.*, 1957, **39**, 193). **Reduction at controlled potential of plutonium (IV). Application to its volumetric determination,** P. Regnaut, J. Corpel and F. Regnaud, 860–869 (in French). **Conductivity of sulphuric acid in the 92 to 98% range,** K. Rosén, 870–879. **Direct polarographic determination of substances with sulphydryl groups in tissues of living organisms,** F. Šantavý and M. Černoch, 880–883 (in German). **A coulometric thickness tester for metal coatings,** G. Sartori and P. Silvestroni, 884 (summary only). **Potentiometric neutralisation titrations with the aluminium electrode,** E. Scarano, 885–891 (in Italian). **The influence of organic solvents on the polarographic half-wave potentials and wave-heights of organic depolarisators,** K. W. Schwabe, 892–904 (in German). **Determination of uranium by high-frequency,** M. T. Silva and A. F. M. Coelho, 905–916 (in French). **The micro-titration of organic compounds. V. Fully automatic unit for the micro-determination of dissociation constants,** W. Simon and E. Heilbronner, 917–923 (in German) (*Chimia*, 1956, **10**, 256). **Integrated current source for automatic**

coulometric titrations. Estimation of chromium and cerium in various solutions, L. E. Smythe, 924–936 (*Analyst*, 1957, **82**, 228). **Separation of certain alkali-metal and alkaline-earth cations by electrochromatography,** G. H. Evans and H. H. Strain, 937–948 (*Anal. Chem.*, 1956, **28**, 1560). **Studies on coulometric cerimetry in organic analysis,** T. Takahashi, 949–963. **Polarographic analysis in the aromatic and heterocyclic series,** J. Tirouflet, 964–970 (in French). **Influence of the kinetics of chemical reactions on polarisation curves. Application to the thiocyanate complexes of titanium (IV) and titanium (III),** S. Tribalat and D. Delafosse, 971–978 (in French). **Coulometric metallometry,** P. S. Tutundžić, 979–986 (in German). **Contributions to the electrochemistry of niobium,** S. Vivarelli, 987–991 (in French). **Simultaneous potentiometric determination of chromium and vanadium,** S. Vivarelli, 992–994 (in French). **Resolution of the pairs Cu - Bi and Cd - In with the object of their polarographic determination,** S. Vivarelli and G. Piccardi, 995–1001 (in French). **Polarographic study of nioxime and the indirect determination of nickel,** P. E. Wenger, D. Monnier and W. Bachmann, 1002–1008 (in French). **Polarographic determination of aldehydes,** J. P. Zwilling, 1009–1016 (in French). **Polarographic determination of physostigmine in pharmaceutical preparations,** A. Anastasi, F. Dal Brollo and E. Mecarelli, 1017–1025 (in Italian). **Polarography of cacao proteins,** V. Bellavita and G. Spagnoli, 1026–1028 (in Italian).

1176. **Precipitations in chemical analysis and the solubility-product principle. I, II.** S. Lewin (South-West Essex Tech. Coll., London). *Lab. Practice*, 1957, **6** (10), 573–576; (11), 642–645.—A discussion is presented, with examples, of the following causes of deviations from behaviour as predicted by the solubility-product theory and values for the usual rapid pptn. in qual. and most quant. analyses—(*i*) absence of exact thermodynamically reversible conditions, (*ii*) use of approximations in deriving the solubility-product equation, and (*iii*) associated equilibria. The applicability of the solubility-product theory is mainly influenced by factor (*i*), but (*ii*) and (*iii*) can also lead to large errors in some instances. W. J. BAKER

1177. **Ethylenediaminetetra-acetic acid and allied compounds in metallurgical analysis.** E. G. Brown. *Metallurgia, Manchr*, 1958, **58**, 149–159.—A survey of literature dealing with specific metallurgical applications is given. (83 references.) J. W. O. PYEMONT

1178. **Analytical note on flavylium perchlorate.** J. Bartos (Services de Recherches Roussel-Uclaf, Paris). *Pharm. Weekbl.*, 1958, **93** (12), 594–596 (in French).—Attention is called to the usefulness of flavylium perchlorate (**I**) (prepared by condensing salicylaldehyde with acetophenone in the presence of acetic acid and $HClO_4$) for colorimetric purposes. A list of organic compounds with which **I** reacts, the colours produced and the sensitivities in μg is given (*e.g.*, malonic acid, methyl- and dimethyl-aniline, indole, 1; aniline and 1-naphthylamine, 2; barbituric acid, pyruvic acid and phenazone, 5). Although these reactions are, on the whole, not very specific, the great sensitivity would nevertheless warrant their use in suitable cases. A. TESSLER

1179. **Disodium ethyl bis-(5-tetrazolylazo)acetate trihydrate. Colorimetric reagent for nickel and copper.** H. B. Jonassen, V. C. Chamblin, V. L. Wagner, jun., and R. A. Henry (Dept. of Chem., Tulane Univ., New Orleans, La., U.S.A.). *Anal. Chem.*, 1958, **30** (10), 1660–1663.—Disodium ethyl di-(5-tetrazolylazo)acetate trihydrate (**I**) forms highly coloured complexes with Ni^{2+} and Cu^{2+}. For Cu^{2+} the pH must be controlled between 5 and 8 and for Ni^{2+} between 6 and 9. **I** has absorption peaks at 270 and 410 mμ, the copper complex at 268, 300 and 535 mμ, and the nickel complex at 335 and 505 mμ. At concn. of 10^{-4} *M* the copper complex has an optical density, in 1-cm cells, of 0·6 at 268 mμ, 0·75 at 300 mμ, and 0·8 at 535 mμ, and the nickel complex has an optical density of 0·25 at 505 mμ at a concn. of 10^{-3} *M*. Absorption maxima are given for 10 common cations. T. R. ANDREW

1180. ***p*-Dimethylaminobenzylidenerhodanine as a colorimetric reagent in inorganic analysis. Colour reactions with metal ions.** Samir K. Banerji and Arun K. Dey (Univ., Allahabad, India). *Chim. Anal.*, 1958, **40** (6), 202–203.—A 0·03% soln. of *p*-dimethylaminobenzylidenerhodanine in acetone is used as a colorimetric reagent. Of the large number of elements treated with it, only Ag, Hg^{II}, Sb, Sn, Au and Fe^{III} show any colour change. J. H. WATON

1181. **Studies on the analytical application of -onium compounds. XIV. Polarographic behaviour of tetraphenylstibonium chloride towards several kinds of metal ion.** Mutsuaki Shinagawa, Hiroshi Matsuo and Hiroshi Okashita (Fac. of Sci., Hiroshima Univ., Hiroshima). *Japan Analyst*, 1958, **7** (4), 219–223.—Tetraphenylstibonium ions (**I**) exhibit two polarographic waves ($E_{\frac{1}{2}} = -0{\cdot}74$ and $-1{\cdot}13$ V *vs.* the S.C.E.); the maximum can be suppressed only with >0·05% gelatin. The height of the first wave is proportional to concn. for $< 6 \times 10^{-3}$ *M*. The first wave is little affected by pH, whilst the second is sensitive to pH change. Since Bi and Hg are pptd. quant. with **I** in the presence of a large excess of KI or KSCN, these are amperometrically titrated in dil. HCl ($\simeq 0{\cdot}1$ *N*) soln. The error is <3%. K. SAITO

1182. **Standardisation of potassium permanganate solution.** Tomoyuki Mukoyama (Fac. of Engng, Yamanashi Univ., Motoyanagi-cho, Kofu). *Japan Analyst*, 1958, **7** (6), 382–385.—Various methods of standardisation of $KMnO_4$ soln. (0·05, 0·1, 0·2 *N*) were compared with a weight burette. The conventional oxalate method gives a higher value by 0·2 to 0·4% than the Fowler and Bright arsenite method (*J. Res. Nat. Bur. Stand.*, 1935, **15**, 493), which appears to be the most accurate. Bright's arsenite method (*Ind. Eng. Chem., Anal. Ed.*, 1937, **9**, 577) is suitable for a rapid determination. K. SAITO

1183. **Reactivity and titration of acid hydrogen in functional analysis.** J. A. Gautier and F. Pellerin (Fac. de Pharm., Paris). *Chim. Anal.*, 1958, **40** (6), 193–201.—Theories of acids and bases are reviewed, and the role of the solvent is stressed. A double factor is seen in the behaviour of acids and bases—an intrinsic factor depending on the

mol. itself and its constituent groups, and an extrinsic factor depending on the solvent. By a suitable choice of solvent, many organic mol. possessing even slightly mobile H atoms may be titrated, alone or in admixture. Details are given of the choice of solvent, titrant and indicator. Examples are quoted of applications of this extended concept of acidimetry to organic chemistry.
J. H. WATON

1184. **Presentation of gas - liquid chromatographic retention data.** D. A. Ambrose, A. M. Keulemans and J. H. Purnell (Chem. Res. Lab., D.S.I.R., Teddington, Middx., England). *Anal. Chem.*, 1958, **30** (10), 1582–1586.—The methods at present in use for presenting retention data are discussed. The use of the known relationships between the elution temp. and either the partition coeff. or the specific retention vol., expressed graphically or in tabular form, is recommended as this offers the only quant. approach to solvent comparison. Because the elution data over a range of temp. are given, the results may then be evaluated for any experimental conditions.
K. A. PROCTOR

1185. **Terms and units in gas chromatography.** H. W. Johnson and F. H. Stross (Shell Development Co., Emeryville, Calif., U.S.A.). *Anal. Chem.*, 1958, **30** (10), 1586–1589.—Terms and units relating to technique, apparatus, reagents, conditions of determination and reporting of results are defined.
K. A. PROCTOR

1186. **Units of measurement in gas chromatography.** W. L. Jones and R. Kieselbach (Engng Res. Lab., E. I. du Pont de Nemours & Co., Inc., Wilmington, Del., U.S.A.). *Anal. Chem.*, 1958, **30** (10), 1590–1592.—A revised set of units based on kinetics is proposed as this makes the recording and interpretation of results more convenient and facilitates quant. evaluation and control of the separation process. The units involved require no correction for pressure drop across the column.
K. A. PROCTOR

1187. **Flame photometry.** H. Aasness. *Medd. Norsk Farm. Selsk.*, 1958, **20** (6), 81–100.—A lecture.

2.—INORGANIC ANALYSIS

General, determination of elements (arranged in the order of the Periodic Table), analysis of minerals and inorganic industrial products.

1188. **Method for the determination of trace impurities.** L. R. Pittwell (Dominion Magnesium Ltd., Haley, Ontario, Canada). *Appl. Spectroscopy*, 1958, **12** (2), 54–57.—Trace impurities are concentrated by complete co-pptn. with a suitable carrier from a soln. of the sample, leaving the matrix metal in soln. The ppt. is dried and analysed spectrographically by complete combustion in an undercut graphite electrode with d.c. arc excitation. Detailed procedures are given for the determination of Al in thorium and its alloys and in ferrosilicon and for impurities in magnesium. Typical sensitivities are—Be and Eu 0·05 p.p.m., Mo, Hf, Sn and Ti 0·01 p.p.m., Ni 0·002 p.p.m., La and V 0·1 p.p.m., Sm 1 p.p.m., and Zr 0·001 p.p.m., all with Al as carrier; Al 0·1 p.p.m. with La as carrier, Hf 1 p.p.m. with Zr as carrier, and Ag 0·0001 p.p.m. with Bi as carrier.
P. T. BEALE

1189. **Studies in fluorimetric analysis. X. Fluorescence properties of various metal oxinate complexes and their use in chemical analysis.** Yasuharu Nishikawa (Chem. Dept., Fac. of Sci., Kyoto Univ., Sakyo-ku). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1958, **79** (8), 1003–1007.—In the solid state, the metal oxinates of groups II, III and IV of the periodic table are fluorescent (light source, mercury lamp) (max. 450 to 650 mμ), the intensity decreasing with increasing atomic number within a given subgroup. The metal oxinates of the Ga group, Al, Y and Zr are extractable from aq. soln. and can be used for fluorimetric analysis.

XI. Fluorescence properties of metal complexes of oxine derivatives and their use in fluorimetric analysis. Yasuharu Nishikawa. *Ibid.*, 1958, **79** (8), 1007–1010.—Similar experiments were carried out with 8-hydroxyquinaldine (**I**), and 5:7-dichloro-, 5:7-dibromo- and 5:7-di-iodo-8-hydroxyquinoline. **I** gives fluorescent complexes with Ag, alkaline-earth elements, Zn, Cd, Ga, In and Zr. The peak of the spectrum is near 480 mμ and the intensity decreases with atomic number within the same subgroup of the periodic table.
K. SAITO

1190. **The separation of ortho-hydrogen and para-hydrogen.** W. R. Moore and H. R. Ward (Massachusetts Inst. Technol., U.S.A.). *J. Amer. Chem. Soc.*, 1958, **80** (11), 2909.—Activated alumina columns, maintained at 77° K, are swept with nitrogen for 35 min. at 190° to 200°. Purified helium is used as the carrier gas. A sharp separation is obtained. Each isomer is positively identified and the homogeneity of the separated components is demonstrated.
K. R. C.

1191. **Analysis for industry [determination of water].** J. H. Thompson. *Ind. Chem. Mfr*, 1958, **34**, 451–453.—Existing methods for the determination of water are surveyed, including absorption techniques, physical methods, extraction methods, and methods based on chemical reaction.
O. M. WHITTON

1192. **Improvements in or relating to a method of determining water in liquids of low water solubility.** Ansul Chemical Co. [Inventors: R. A. Line and H. Hoftiezer]. Brit. Pat. 805,012; date appl. 20.3.56. —The concn. of moisture in dichlorodifluoromethane and similar refrigerant liquids, or in petrol or fuel oil, is determined by means of indicating material consisting of pure anhyd. cobaltous bromide uniformly distributed, at the rate of 0·01 to 0·7 g per cu. cm, in white unsized cellulosic material (strips of paper, average thickness 0·007 in.). The change in colour of a strip of the material when immersed in the liquid under test is compared with the colours of standard strips.
J. M. JACOBS

1193. **Improvement in the determination of heavy water by means of the thermal conductivity method.** Saburo Yanagisawa, Michiharu Seki, Yoshikazu Watanabe, Shigeru Nakamura and Fumio Morita (Fac. of Engng, Keio Univ., Koganei, Tokyo). *Japan Analyst*, 1958, **7** (5), 301–304.—The accuracy of the thermal conductivity method for the determination of a low concn. (<0·05%) of heavy water is improved (accuracy, ±0·02%) by the use of a thermistor and by cooling the cell with ice in a sealed vessel with the thermistor. Purified vapour is heated at 400° for 15 min. in the presence of pure zinc and platinum, and the resulting gases are introduced into the cell to give a pressure of 150 to 180 mm (Hg).
K. SAITO

1194. **Quantitative determination of water of crystallisation in certain crystallohydrates by absorption in the near infra-red (0·8 to 2·5 μ).** D. S. Gorbenko-Germanov, R. A. Zenkova and T. L. Bolotina. *Zhur. Anal. Khim.*, 1958, **13** (5), 590–594.–Water of crystallisation may be determined by its i.r. absorption at 5130 cm^{-1}, but this band may be displaced by 100 to 200 cm^{-1}. The absorption is measured in compressed tablets of KCl 0·55 ± 0·01 mm in thickness, weighing 117 mg and containing milligram amounts of the crystals. A calibration curve is constructed from tablets containing 0·5 to 21·1 mg of $Eu_2(SO_4)_3.8H_2O$. The optical density is calculated from the formula $D = \log I_0/I$, where I_0 and I are the transmissions of the KCl tablet and the sample tablet, respectively. A method is described for calculating the optical density at the three extreme points, *i.e.*, the points of max. transmission at each end of the absorption max., and that of the absorption max. itself. The water of crystallisation was determined in the following hydrates—$KEu(SO_4)_2.H_2O$, $KEu(SO_4)_2.2H_2O$, $K_3Eu(SO_4)_3.H_2O$, $Nd_2(SO_4)_3.5H_2O$, $Nd(OOCCH_3)_3.H_2O$ and $CaSO_4.2H_2O$.

C. D. KOPKIN

1195. **Determination of lithium and sodium chlorides by potentiometric titration following 2-ethyl-1-hexanol separation.** G. R. Waterbury, E. H. van Kooten and B. Morosin (Univ. of Calif., Los Alamos Sci. Lab., N.M., U.S.A.). *Anal. Chem.*, 1958, **30** (10), 1627–1629.—Lithium is separated from Na by double extraction of the chlorides with 2-ethylhexanol at 140°. The filtered extract is diluted fourfold with acetone or dioxan and titrated potentiometrically with 0·4 *M* $AgNO_3$. A glass reference electrode and a silver - silver chloride indicator electrode are used. Sodium may be determined by titration of the residue insol. in 2-ethylhexanol. The interference of 21 ions is studied.

T. R. ANDREW

1196. **Flame-photometric determination of small amounts of potassium in sodium and its compounds after enrichment with ammonium tetraphenylboron.** K. H. Neeb and W. Gebauhr (Forschungslab. der Siemens-Schuckertwerke A.-G., Erlangen, Germany). *Z. anal. Chem.*, 1958, **162** (3), 167–174.—Treat an aq. soln. of the sample (containing >1 μg of K) at pH 4·5 with ammonium tetraphenylboron, filter, dissolve the ppt. in 40% aq. tetrahydrofuran, burn in the oxy-hydrogen flame and measure the emission at 770 mμ. If the ratio Na:K is very large (*e.g.*, >20,000:1), perform a second pptn. of K tetraphenylboron from acetone soln. before the flame photometry. The mean error is $\simeq \pm 5\%$.

A. R. ROGERS

1197. **Gravimetric determination of copper with *m*-nitrobenzaldoxime.** E. Papafil, M.-A. Papafil and D. Furnică (Univ. "A. I. Cuza," Iaşi, Romania). *An. Ştiinţ. Univ. "A. I. Cuza," Iaşi*, 1957, **3** (1–2), 295–301.—The use of *m*-nitrobenzaldoxime as reagent for the determination of Cu in the presence of Na^+, K^+, NH_4^+, Ca^{2+}, Ba^{2+}, Sr^{2+}, SO_4^{2-}, NO_3^-, Cl^- and CH_3COO^- is proposed. *Procedure*—To the cold aq. soln. containing 0·02 to 0·06 g of Cu is slowly added just sufficient aq. NH_3 to give a clear soln. A hot soln. of the reagent containing 2 to 3 times the theoretical required amount is added in small amounts at a time, with continuous stirring. An amorphous green ppt. is formed immediately, which agglomerates in 5 to 10 min. when stirred vigorously on a hot brine bath, leaving a clear supernatant liquid. The ppt. is collected in a sintered glass crucible under vacuum, washed with water and diethyl ether, and dried at 110° to 115° to constant wt. For good results the soln. should not be too concentrated; the soln. of the reagent must be much more dilute than that of the Cu^{2+} and should be added very slowly with vigorous agitation. The final vol. should be between 75 and 150 ml. It is claimed that the max. error is ±0·3%.

H. SHER

1198. **Spectrophotometric determination of ultra-micro amounts of copper with 1:5-diphenylcarbohydrazide [*sym.*-diphenylcarbazide].** R. W. Turkington and F. M. Tracy (Wesleyan Univ., Middletown, Conn., U.S.A.). *Anal. Chem.*, 1958, **30** (10), 1699–1701.—In basic soln. Cu^{2+} react with *sym.*-diphenylcarbazide to give an intense colour (molar absorption index 158,800 at 495 mμ, pH 9). The intensity increases with increasing pH and the pH must be controlled accurately for quant. work. Of 19 cations and 23 anions studied for interference, Cr^{3+} interferes seriously at concn. similar to that of Cu^{2+}; Cd^{2+}, Mn^{2+}, Co^{2+} and Hg^{2+} can be tolerated at concn. similar to that of Cu^{2+}; and the other ions studied can be tolerated at much higher concn. The copper complex is sol. in benzene and *iso*amyl alcohol and may be extracted by these solvents.

T. R. ANDREW

1199. **Co-precipitation [of copper] in the system basic dye - metal ion - halide.** E. M. Strel'tsova and V. I. Petrashen'. *Trudy Novocherk. Politekh. Inst.*, 1958, **69/83**, 153–154; *Ref. Zhur., Khim.*, 1958, (19), Abstr. No. 64,177.—To separate 10^{-7} to 10^{-4}% of Cu from soln., it is co-pptd. with the iodide or thiocyanate of methyl violet in the form [methyl violet]$^{m+}$ $[CuY_n]^{m-}$, where Y is I^- or SCN^-. It is established that 97 to 100% of the Cu is pptd. from a soln. containing 1 to 5 μg of Cu in 200 ml at an acidity >0·1 *N* in H_2SO_4 or HCl, with concn. of NH_4SCN >0·020 mole per litre or of NH_4I >0·033 mole per litre, and with addition of a 1% soln. of methyl violet. The ions Fe^{3+}, Cd^{2+}, Ni^{2+}, Ag^+, Zn^{2+}, Sb^{3+} and Sn^{2+}, which also co-precipitate, are first removed by an analogous method in the presence of free iodine, after which the excess of iodine is reduced with hydroxylamine hydrochloride and the Cu co-pptd. The study was carried out by using the radioactive isotope ^{64}Cu.

C. D. KOPKIN

1200. **Use of oxalic acid in analytical chemistry. VII. Separation and determination of copper in the presence of iron.** Tamotsu Matsumoto (Fac. of Sci., Okayama Univ., Tsushima). *Japan Analyst*, 1958, **7** (6), 346–350.—The co-pptn. of Fe^{3+} with Cu oxalate becomes appreciable when the concn. of Fe^{3+} is >0·5 mole per mole of Cu in 40% (v/v) acetic acid. The amount of oxalic acid must be increased to make the molar ratio of this acid to the sum of Cu plus Fe > 2. In place of acetic acid, a mineral acid can be used, provided that the pH of the soln. is adjusted to the same value. No interference results from alkali metals, as long as the alkali oxalate remains in soln.

VIII. Separation and determination of copper in the presence of cadmium, arsenic or aluminium. Tamotsu Matsumoto. *Ibid.*, 1958, **7** (6), 350–354.—In the presence of <0·5 mole of Cd, As or Al, the separation of Cu is satisfactory if the concn. of the Cu is greater than twice that of the sum of the metals.

K. SAITO

1201. **Polarographic determination of copper and iron and its application in the hydrometallurgy of copper.** K. J. Cathro and A. Walkley (Div. Ind. Chem., C.S.I.R.O., Melbourne, Australia). *Aust. J. Appl. Sci.*, 1958, **9** (2), 105–114.—Procedures are given for the polarographic determination of Cu and Fe in samples from the roasting, leaching and electrolysis of sulphide ores. Provided that the ratio of Cu to Fe is between 100 and 0·05, the two elements can be determined together in 0·01 to 0·05 *M* 1:2-diamino*cyclo*hexanetetra-acetic acid (**I**) with *M* to 2 *M* ammonium acetate as supporting electrolyte ($E_{\frac{1}{2}} = -0{\cdot}16$ V for Fe and $-0{\cdot}55$ V for Cu). When the ratio of Fe to Cu is >20, the electrolyte is 0·2 *M* pyridine - 0·2 *M* pyridinium chloride with 0·005% basic fuchsine as suppressor for the higher wave of Cu, $E_{\frac{1}{2}} = -0{\cdot}29$ V being measured. If much Bi and Pb are present, Fe should be extracted with di*iso*propyl ether and the Cu and Bi polarograms can then be obtained in **I** - ammonium acetate - acetic acid as supporting electrolyte. In leachate samples, Fe^{3+} can be determined in a 5% H_2SO_4 - saturated salicylic acid electrolyte against a mercury $|Hg_2SO_4|$ saturated K_2SO_4 anode, whilst Cu alone can be determined (in ≃15 min.) in 4 *M* aq. NH_3 - 0·3 *M* NH_4Cl buffer (to ensure complete pptn. of Fe^{3+}) with 1% aq. Na_2SO_3 as de-oxygeniser. Results given by all these methods agree well with those of the usual volumetric and gravimetric procedures.

W. J. Baker

1202. **The identification and determination of copper and cobalt in the presence of large quantities of iron by paper chromatography.** M. Sterescu and N. Keim. *Rev. Chim., Bucharest*, 1958, **9** (6), 329.—The separation is based on the R_F values of Co, Cu and Fe which are, respectively, 0·09, 0·30 and 0·92. *n*-Butanol - conc. HCl (85:15) is used as developer.

H. Sher

1203. **Electroanalysis with the use of EDTA. I. Electrolytic determination of copper in the presence of antimony and arsenic.** Hisao Hayakawa (Fac. of Education, Kobe Univ., Sumiyoshi-cho, Higashinada-ku). *Japan Analyst*, 1958, **7** (6), 360–362.—The electrolytic deposition of Cu (<0·1 g) in NH_4NO_3 soln. (≃1 g per 150 ml of electrolyte) containing hydroxylamine hydrochloride (2 g) and EDTA (>twice the wt. of the Cu) is quantitative at pH ≃3·1. When the soln. is electrolysed at $-0{\cdot}36$ to $-0{\cdot}40$ V *vs.* the S.C.E., the presence of <15 mg of Sb^{III} does not cause interference, and As^{III} (>1 mg) is deposited with the Cu. When the applied potential is $-0{\cdot}33$ V, As^{III} (<24 mg) is not deposited, but the time taken for the deposition of Cu is ≃4·5 hr. (longer for a larger amount). When As is oxidised to As^{V} with Br or $KMnO_4$, Cu can be electrolytically determined without the use of the controlled potential technique.

K. Saito

1204. **Constant-current potentiometric titration of copper, lead and cadmium at a semi-convection mercury electrode.** Nobuyuki Tanaka and Yasuhiko Sakuma (Fac. of Sci., Tohoku Univ., Katabira-cho, Sendai). *Japan Analyst*, 1958, **7** (4), 223–228.—A semi-convection mercury electrode (the electrolytic soln. is stirred constantly over a mercury cathode, which is placed in the middle of a cell) was used as an indicator electrode in the constant-current potentiometric titration of Cu, Pb and Cd with EDTA (disodium salt). The sensitivity is so superior to that of the dropping-mercury electrode that the linear relationship between the concn. and the limiting current holds for concn. of $< 10^{-4}$ *M*. In an acetate buffer, Cu, Pb and Cd (at pH 4·2, 4·2 and 5·2, respectively) ($>4 \times 10^{-5}$ *M*) are titrated with EDTA with an average deviation of 2% (residual current, 0·8 μA for Cu, ≃1·3 for Pb and 2 to 3 for Cd; applied current, 1 to 3 μA for each). The titration curve is in accord with the formula of Tanaka *et al.* (*Anal. Chem.*, 1956, **28**, 1555).

K. Saito

1205. **Volumetric method for the determination of small amounts of silver in presence of large amounts of copper and nickel.** K. C. Seal (Gov. Test House, Alipore, Calcutta). *J. Indian Chem. Soc.*, 1958, **35** (6), 453–454.—The determination of Ag by titrating with iodine - iodide soln., with starch as an internal indicator, is carried out in the presence of an excess of Na acetate or $NaHCO_3$. The end-point is sharper in the Na acetate buffer medium. Both iodine and iodide enter into the reaction and the iodine - iodide soln. is standardised against a known $AgNO_3$ soln. Copper and Ni do not interfere.

I. Jones

1206. **Studies in paper chromatography. I. Separation of silver, lead and mercury(I) by the use of inorganic salt solutions as developers.** Hiromu Imai (Fac. of Engng, Kansai Univ., Ooyodo-ku, Osaka). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1958, **79** (6), 651–654.—The paper-chromatographic behaviour of Ag, Pb and Hg^{I} was examined with various acid (0·1 *N* HCl, 0·35 *N* H_2SO_4 and 0·65 *N* HNO_3), basic (*N* NaOH, 3·8 *N* aq. NH_3, 2 *N* Na_2CO_3 and 2 *N* K_2CO_3) and neutral (*M* NaCl, KCl, NH_4Cl, KI, Na_2SO_4, $NaVO_3$, NH_4SCN and Na_2SO_3) aq. soln. Little change in R_F was observed with variation in the concn. of acid and alkali, and attempts to separate the spots of the metals mentioned were unsuccessful. Among inorganic salts, 0·2 *N* Na_2SO_3 gives satisfactory results (R_F, 0·74 to 0·60 for Ag^+, 0·03 to 0·01 for Pb^{2+}, and 0·83 to 0·75 for Hg_2^{2+}; the value changes with the concn. of the metal ions). When Hg is oxidised to Hg^{2+}, the spots can be separated with *N* HCl, *M* NH_4Cl, KCl or NaCl, the R_F being ≃0·85 for Hg^{2+}, ≃0·73 for Pb^{2+}, and ≃0 for Ag^+.

K. Saito

1207. **Radiochemical procedure for beryllium.** J. D. Buchanan (Tracerlab, Inc., Western Division, 2030, Wright Avenue, Richmond, Calif.). *J. Inorg. Nuclear Chem.*, 1958, **7** (1–2), 140–142.—A procedure is described for the separation of Be from fission products and U. It includes the passage of the Be with beryllium carrier in 9 *M* HCl through a column of Dowex 1X-10 (H form), pptn. of $Fe(OH)_3$ from a strongly alkaline soln. of the Be, and the threefold extraction of Be acetylacetonate into benzene. The Be is finally ignited to BeO, weighed and counted.

G. J. Hunter

1208. **Chemical analysis by the use of EDTA. V, VI. Separation of beryllium from other metals including aluminium by an ion-exchange resin.** Tomitsugu Taketatsu (Chem. Dept., Fac. of Sci., Kyushu Univ., Hakozaki, Fukuoka). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1958, **79** (5), 586–590; 590–594.—When a column (diameter 7 mm, length 11·5 mm) of Amberlite IR-112 (70 to 100 mesh) is eluted with 0·5% EDTA soln. of pH 3·7 (ammonium nitrate buffer) at a flow rate of 1·0 to 1·5 ml per min., Cu, Zn, Cd, Pb, Co, Ni and Th (<100 mg each) are eluted with 100 ml of eluent, and Mn, Ce and U with 500 ml. Ferric iron is eluted with 0·5% EDTA

soln. of pH 3·0 (400 ml), whereas Ti, Cr, Al and Be remain on the column throughout these elutions. When a buffer soln. (pH 3·5 to 5·0 at 12°) containing Be, Al, Cr, Ti and a slight excess of EDTA is passed through the column (NH_4^+ form) at the same flow rate, only Be is adsorbed on the resin. At a higher temp., the adequate pH range decreases (*e.g.*, at 30°, 3·3 to 3·8). The Be is readily eluted with 3 *N* HCl (100 ml). By the combination of these two procedures, satisfactory separation of Be (< 50 mg) can be carried out. K. SAITO

1209. **Determination of calcium in wolframite concentrates by fluorescent X-ray spectrography.** W. J. Campbell and J. W. Thatcher. *Rep. Invest. U.S. Bur. Min.*, 1958, No. 5416, 18 pp.—Wolframite concentrates should have a calcium concn. > 0·2% (as carbonate, phosphate or tungstate). Particle size is reduced by grinding, chemical fusion with Na_2CO_3 or by solution in acid. X-ray spectrographic analysis is accurate to ±5% in calcium concn. > 0·3%, ±10% at a 0·1% level, and has a lower limit of detectability of 0·005 to 0·01%. The operating characteristics of a gas-flow proportional counter used with a pulse-height analyser are studied. This detector is considered very efficient for Ca K_α radiation, but is of low efficiency for overlapping higher-order radiation, being equivalent to Geiger tubes. S.C.I. ABSTR.

1210. **Chemical analysis of cupola slags. II. Determination of calcium and magnesium oxides.** W. E. Clarke (B.C.I.R.A. Chemical Laboratory, Alvechurch, Birmingham). *J. Res. Brit. Cast Iron Ass.*, 1958, **7** (5), 249–256.—Results are presented of an investigation into the conditions for the complexometric titration of Ca and Mg and various methods (including masking, separation by pptn., ion exchange, and solvent extraction) of overcoming the interference due to Fe, Al and Mn. Solvent extraction was found to be the most satisfactory method, and for slags with a low magnesium content the cupferron method is recommended. The sample (1 g) is heated gently with 15 ml of $HClO_4$ (sp. gr. 1·54), 15 ml of HNO_3 (sp. gr. 1·42) and 5 ml of HF until the reaction is complete, adding further HF if necessary. The soln. is evaporated to fumes of $HClO_4$ and then allowed to fume gently for 5 min., but is not taken to dryness. The residue is diluted with water to 200 ml and two 20-ml aliquots are shaken with 2 ml of glacial acetic acid, 10 ml of 2 *M* Na acetate and 10 ml of 6% cupferron soln. After extraction with 20 ml of $CHCl_3$ and addition of a further 1 ml of cupferron soln., the extraction is repeated with 10 ml of $CHCl_3$, 5 ml of Na diethyldithiocarbamate (100 g per litre) is added and extraction with 10-ml portions of $CHCl_3$ is continued until the $CHCl_3$ layers are colourless. Calcium and Mg are determined in the aq. layer by complexometric titration. For slags with a high magnesia content, acetylacetone is substituted for the cupferron. J. M. JACOBS

1211. **Interpretation of vaporisation-, decomposition- and excitation-processes in flames. The influence of silicic and phosphoric acids and aluminium on the flame-photometric determination of alkaline earths.** W. Schuhknecht and H. Schinkel (Ensheimerstr. 35, St. Ingbert/Saar, Germany). *Z. anal. Chem.*, 1958, **162** (4), 266–279.—A flame photometer constructed by Schuhknecht, which can be used with propane - air, H - air, H - O or acetylene - air, was used for most of the work in conjunction with either the Beckman or Zeiss flame spectrophotometer. For the latter H - O only was used. The interference of silicic acid, sodium silicate, H_3PO_4 and various aluminium salts on the flame-photometric determination of Ca was examined in detail. The interference caused by Al was not affected by the nature of the anion. All interferences were reduced by the use of two atomising chambers and a higher temp. The mechanism of interference is explained by a vaporisation block caused by the formation of only slightly volatile compounds. A detailed method for the flame-photometric determination of Ca in the presence of these interfering substances is described. All solutions contain 1 g of $SrCl_2.6H_2O$ per litre. S. BAAR

1212. **Co-precipitation of zinc with pyridine-containing complex compounds.** I. M. Korenman and Z. I. Glazunova (N. I. Lobachevskiĭ Gor'ki State Univ.). *Zhur. Anal. Khim.*, 1958, **13** (5), 528–532.—The co-pptn. of Zn with $[MPy_2]X_2$, where M is Cu^{2+}, Cd^{2+} or Ni^{2+} and X is SCN^- or Br^-, is studied by the use of ^{65}Zn. The graphs constructed on the co-ordinates log (Zn^{2+} content in μg per mg of ppt.) and log (M^{2+}/Zn^{2+} in the starting soln.) are straight lines which are approximately parallel, and have negative slopes. Increase of temp. greatly lowers the amount of co-pptd. Zn, thus allowing Cu to be separated from Zn by pptg. $[CuPy_2](SCN)_2$ at 100° and micro amounts of Cu to be determined. The pptn. is effected by adding a 1% soln. of NH_4SCN (1 ml) and a 10% soln. of pyridine (0·5 ml) to 1·5 ml of soln. 0·25 *N* in HNO_3. To determine Cu, wash the ppt. with 1% pyridine soln., dissolve it in the minimum quantity of *N* HNO_3 and titrate with 0·1 *N* $AgNO_3$ from a micro-burette in the presence of ferric ammonium sulphate. C. D. KOPKIN

1213. **Use of amperometry in the phase analysis of zinc compounds in ores and enrichment products.** N. I. Solntsev and R. I. Chudina. *Sb. Nauch. Trud. Gos. Nauch.-Issled. Inst. Tsvet. Met.*, 1958, (14), 103–111; *Ref. Zhur., Khim.*, 1958, (19), Abstr. No. 64,188.—A procedure is described for the amperometric determination of all forms of Zn. The amperometric titration is carried out with 0·05 or 0·1 *N* $K_4Fe(CN)_6$ with a platinum electrode with anodic polarisation and a rate of rotation of ≃700 r.p.m.; external potential +0·7 V; a N.C.E. is used as comparison electrode. The initial vol. of the soln. is 50 ml. The total content of Zn in ores (or flotation tails) is determined by amperometric titration in an ammoniacal citrate medium. The Zn in calamine and adamite is selectively dissolved in 0·13 *M* tartaric acid and, after oxidation of Fe^{2+} with dichromate, the Zn is titrated amperometrically in an ammoniacal acetate or (for significant amounts of Fe) in an ammoniacal citrate medium; no interference is caused by Fe^{3+}, Cu or Pb. The Zn in smithsonite is dissolved by treating the residue after the extraction of calamine and adamite with Löwe's [?] mixture, and the Zn in the soln. is determined polarographically (the presence of large quantities of ammonium salts interferes in the amperometric titration of Zn). Dissolve the Zn of descloizite in 0·12 *N* HCl and titrate the Zn amperometrically in an ammoniacal acetate or ammoniacal citrate medium; V does not interfere. Dissolve the Zn in sphalerite by treating the residue after solution of descloizite with acidified 0·1 *M* $FeCl_3$ and titrate Zn amperometrically in an ammoniacal citrate medium. The determination of Zn in the

residual material is also carried out amperometrically in an ammoniacal citrate medium. If the ore contains adamite, treat a separate sample with a 5% soln. of $CuSO_4$ (dissolving the Zn of calamine and smithsonite) and, after pptn. of Cu from the resulting soln. with metallic Al, determine Zn by amperometric titration in an ammoniacal citrate medium; the Zn in adamite is found by difference. In all cases the results obtained agree well with those of the polarographic method. By replacing the polarographic determination by amperometric titration, the time required for the phase analysis is considerably shortened. C. D. KOPKIN

1214. **New rapid gravimetric method for the determination of cadmium. II. Use of 1-allylthiocarbamoyl-2-thiocarbamoylhydrazine.** E. Popper, L. Popa, V. Iunie and L. Roman (Pharm. Faculty, Cluj, Romania). *Rev. Chim., Bucharest*, 1958, **9** (6), 300–302.—To a warm soln. of Cd^{2+} is added 1 to 2 g of NH_4Cl and, gradually, an excess of a 1% ethanolic soln. of the reagent equivalent to approx. ten times the quantity of cadmium salt taken. The soln. is buffered to pH 6 with 1 to 2 g of Na acetate, and allowed to precipitate for 20 min. The white ppt. is filtered off hot, washed with hot H_2O, then with warm 95% ethanol and ether and finally dried *in vacuo*. It is claimed that a determination takes 45 min., that accuracy lies between +0·34 and −0·43%, and that sensitivity is up to 6 μg per ml. The method can be used in the presence of alkali metals and for estimations of Cd in the alkaline earths, but heavy metals interfere.

III. Use of a mercaptan reagent. E. Popper, L. Popa, V. Iunie and L. Roman. *Ibid.*, 1958, **9** (6), 302–305.—A 1% ethanolic soln. of 5-anilino-2-mercapto-1:3:4-thiadiazole is used; it gives a white cryst. ppt. with Cd^{2+}. *Procedure*—A soln. of Cd^{2+} is treated with 10 ml of ethanol and warmed on a water bath. The reagent is then added dropwise with continuous stirring, and the ppt. allowed to settle for 15 to 20 min., the beaker being covered to prevent evaporation of ethanol and the deposition of reagent. If the Cd salt was of a strong acid, the soln. should be buffered with Na acetate. The ppt. is washed with warm 50% ethanol, then with 95% ethanol and ether, and vacuum-dried. It is claimed that the accuracy is ±0·3%; the determination requires only 45 min. and Cd can be estimated in the presence of alkali metals and alkaline earths. H. SHER

1215. **Quantitative determination of uni- and bi-valent mercury by means of 1-phenylthiosemicarbazide.** N. V. Koshkin (Leningrad Technol. Inst. Foodstuffs Ind.). *Zhur. Anal. Khim.*, 1958, **13** (3), 308–310.—Both Hg^{I} and Hg^{II} can be determined. Copper nitrate is used as an indicator and an intensely blue coloration due to formation of a soluble complex is observed. When the solutions are concentrated a dark-blue coloration and sometimes a ppt. is observed. Titration can be carried out in an acid medium over a wide pH range. A measured volume of acetic acid soln. of 1-phenylthiosemicarbazide of a known concn. is taken with 2 to 3 drops of 0·1 *N* $Cu(NO_3)_2$; this soln. is titrated with $Hg(NO_3)_2$ soln. until the blue colour changes to yellow. W. ROUBO

1216. **Loss of boron by volatilisation during its determination.** Shigeo Wakamatsu (Toto Seiko Co., Minamisuna-machi, Koto-ku, Tokyo). *Japan Analyst*, 1958, **7** (5), 309–313.—No appreciable loss of B was observed from samples heated with HCl, HNO_3, H_2SO_4 or aqua regia, even after heating for 10 hr. with fuming H_2SO_4 in a current of air or on evaporation to dryness with aqua regia. By these procedures, however, boric acid is converted into a form that is inactive towards carmine. K. SAITO

1217. **Colorimetric determination of small quantities of boron with carmine.** G. Pitulescu. *Rev. Chim., Bucharest*, 1958, **9** (6), 318–319.—*Procedure*—The finely pulverised sample (1 to 0·01 g) is treated in a quartz crucible with 5 ml of Ca saccharate soln. After evaporating to dryness, the residue is decomposed gently in an electric furnace and calcined at 900° until the carbon is oxidised (approx. 15 min.). The residue is treated with 5 ml of conc. H_2SO_4, collected in a sintered glass filter and washed several times with conc. H_2SO_4. The filtrate is made up to known vol. with H_2O, and treated with 10 ml of a soln. of carmine (0·05% in conc. H_2SO_4). After 45 min. the colour is compared with that of standard samples. It is claimed that the method can be used with waters, rocks and minerals. H. SHER

1218. **The determination of boron in silicon.** V. Barcanescu and H. Minasian. *Rev. Chim., Bucharest*, 1958, **9** (6), 316–318.—The basis of the method is the blue coloration obtained with boron and carmine after separation from silica by distilling off the boron as methyl borate. It is claimed that by this procedure between 0·0005 and 0·25 g of B can be determined in 100 g of silicon; with a spectrophotometer, down to 0·2 μg of B per g of silicon can be determined. H. SHER

1219. **Determination of boron in aluminium-uranium fuel elements. Application of the carminic acid spectrophotometric method.** K. W. Puphal, J. A. Merrill, G. L. Booman and J. E. Rein (Atomic Energy Division, Phillips Petroleum Co., Idaho Falls, U.S.A.). *Anal. Chem.*, 1958, **30** (10), 1612–1614.—The procedure of Hatcher and Wilcox (*Anal. Chem.*, 1950, **22**, 567) has been applied to the determination, without separation, of B in Al-U alloys. Uranium is without effect on the determination, but Al gives a slight positive error (100 mg of Al ≡ ≃0·03 mg of B), corrected for by a blank determination on Al-U alloys, B-free, of similar general composition to the sample. Concn. of 1% of Fe, 0·2% of Cu, 0·1% of Mn and 0·05% of Cr, Ni, Ti or Zn in the sample are without effect. *Procedure*—Dissolve 0·5 to 2 g under reflux in HCl-H_2O (10 ml + 15 ml per 1 g of sample). When dissolution is almost complete add H_2O_2 (2 ml of 30% per 1 g of sample) and boil under reflux to remove excess. Cool and dilute to 40 times the sample wt. (g). Filter, and store in polyethylene vessels. If the sample contains B as B_4C, dissolve the sample (containing 1 to 5 mg of B) in HCl and H_2O in a silica beaker in the presence of 1 g of ashless cellulose paper, and filter off the undissolved B_4C with a No. 42 paper. Ash the ppt. in a platinum crucible and fuse with 4 g of Na_2CO_3. Dissolve the melt in H_2O, acidify with 20 ml of HCl and dilute to 100 ml. Boron-impregnated polyethylene-tape samples are slowly burned in platinum and the ash is fused with 0·5 g of Na_2CO_3. Continue as for B_4C-containing samples. An aliquot of the diluted samples, containing 0·01 to 0·07 mg of B, is transferred to a 25-ml flask and H_2O is added to make a total volume of 2·0 ml. Add 2 drops of HCl, cool in an ice bath and add cold H_2SO_4 (10 ml). Shake until gas evolution ceases, remove from ice bath and allow to reach room

temperature. Add 10 ml of carminic acid (0·05% in 96% H_2SO_4), set aside for 1 hr., dilute to 25 ml with H_2SO_4 and measure the extinction at 580 mμ. Compare with a blank determination. A standard deviation of ±1·4% is claimed. T. R. ANDREW

1220. **Micro-determination of aluminium in calcium.** H. Ostertag and Y. Cappelliez. *Compt. Rend.*, 1958, **246** (10), 1550–1553.—From 5 to 200 p.p.m. of Al in metallic calcium can be determined to within ±2 p.p.m. by measuring the extinction of a colloidal suspension of Al cupferronate pptd. at pH 2. *Procedure*—Dissolve the sample (≃1·3 g) in H_2O (65 ml), neutralise the soln. with warm 2 *N* HCl and make the vol. up to 100 ml with H_2O. To an aliquot (≡200 to 400 mg of Ca^{2+}) add 0·02 *N* HCl (4 ml) and cupferron soln. (5 ml), and adjust the vol. to 50 ml. Stir the mixture and, after allowing it to remain for 70 min. in darkness, add 0·1% gelatin soln. (2 ml) before measuring the extinction at ≃400 mμ in a 2-cm cell. Beer's law is valid up to ≃50 μg of Al. W. J. BAKER

1221. **Rapid determination of alumina content of clays and bricks with Complexone. I.** G. de Longuyon (Martin & Pagenstecher A.-G., Köln-Mülheim, Germany). *Ber. dtsch. keram. Ges.*, 1958, **35** (5), 155–158.—In acid soln., all but the alkali and alkaline-earth ions form a complex with EDTA (disodium salt) (**I**). Excess of **I** added to the soln. is titrated with Zn acetate soln. and an excess of NaF is added which forms $3NaF.AlF_3$ and an amount of **I** equiv. to the Al_2O_3 content is liberated and titrated. It is unnecessary to separate the SiO_2. *Procedure*—The sample (1 g) is fused with NaOH in a nickel crucible and the melt is dissolved, acidified with HCl and made up to 250 ml. To 50 ml of this soln., diluted to 200 ml, an excess (20 ml for 40% of Al_2O_3) of 0·1 *N* **I** is added and, after heating to 30° to 40°, the soln. is neutralised with aq. NH_3 and made just red to phenolphthalein with HCl. Acetate buffer soln. (pH 6 to 6·5) (20 ml) is added and the soln. boiled for 3 min. The excess of **I** is titrated with 0·1 *N* Zn acetate to the blue colour of benzidine - ferro - ferricyanide indicator. Saturated NaF soln. (30 ml) is added and, after boiling for 3 min., the cold soln. containing the liberated **I** is titrated as described above. Any TiO_2 present (determined with H_2O_2) forms K_2TiCl_6 (which does not react with **I**) and only if its content is > 4% is it necessary to apply a correction. The analysis is completed in 3 hr. J. A. SUGDEN

1222. **Cosmic-ray-induced radioactivities in meteorites. I. Chemical and radiometric procedures for aluminium, beryllium and cobalt.** W. D. Ehmann and T. P. Kohman (Carnegie Inst. Technol., Pittsburgh). *Geochim. et Cosmoch. Acta*, 1958, **14** (4), 340–363.—The separation and purification of Al, Be, Fe and Co from iron and stone meteorites, tektites, and terrestrial silicate materials is described. The main objective is radiochemical purity of the isolated radio-elements; ion-exchange and solvent-extraction techniques are used whenever possible because of their high specificity and applicability. Aluminium-26 and ^{10}Be are prepared for counting in the form of Al_2O_3 and BeO; ^{60}Fe is detected by extraction of its active daughter ^{60}Co, counted as CoS. The identity of a radionuclide is established by the criterion of constant specific activity on re-cycling the sample through the chemical purification procedure. Details are given of the construction of special low-background counters for the detection and measurement of feeble amounts of beta emitters in the form of small solid samples. In routine operation, 3 to 4-day backgrounds are alternated with 6 to 8-day sample counts yielding a lower counting rate limit of 0·017 counts per min. With counting yields of 40% and specimen sizes of 100 g it is possible in favourable cases to detect radio-nuclides at a specific activity of 0·0004 disintegration per min. per g of sample. R. A. HOWIE

1223. **Colour reactions of gallium and indium salts with organic reagents.** N. S. Poluektov and N. K. Kiseleva (Inst. of Gen. and Inorg. Chem., Acad. Sci., Ukr. SSR, Laboratories in Odessa). *Zhur. Anal. Khim.*, 1958, **13** (5), 555–561.—The colour reactions of Ga, In and Al with dihydroxy azo dyes, Schiff's bases, phenylfluorone derivatives and diphenylcarbazone are studied, as well as colour reactions for In based on the formation of complex anions. C. D. KOPKIN

1224. **Studies in fluorimetric analysis. IX. Fluorimetric determination of gallium with 5:7-dihalo-oxines.** Yasuharu Nishikawa (Chem. Dept., Fac. of Sci., Kyoto Univ., Sakyo-ku). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1958, **79** (5), 631–637.—The Ga complexes of 5:7-dichloro- (**I**), 5:7-dibromo- (**II**) and 5:7-di-iodo-8-hydroxyquinoline (**III**) are extracted with $CHCl_3$ (3 × 10 ml) from ammonium acetate buffer (≃50 ml) of pH 3·2 to 3·3. The fluorescence (max. 545, 540 and 550 mμ for the complexes with **I**, **II** and **III**, respectively) of the $CHCl_3$ soln. is proportional to the amount of Ga (<10 μg per 50 ml of $CHCl_3$). When **I** is used, Al, Ti, Mo, Fe, V and a large amount (>100 μg) of Cu and W interfere. Reduction with hydroxylamine hydrochloride (**IV**) eliminates the influence of Fe and V. Gallium is extracted with ether (20 ml) from 6 *N* HCl soln. (30 ml), the ether layer is evaporated to dryness, the residue is dissolved in *N* HCl (8 ml), and made up to 50 ml after the addition of **IV** (2 g), 20% ammonium acetate soln. (5 ml) and **I** (0·2%, 0·25 ml). The pH is adjusted and the Ga extracted with $CHCl_3$. K. SAITO

1225. **Detection of a micro amount of indium with an anion exchanger and alizarin red S.** Kiyoshi Katou and Hidetake Kakihana (Nogoya Shiritsu Kogyo, Nakagawa-ku, Nagoya). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1958, **79** (6), 762–767.—The detection of In with alizarin red S (**I**) becomes very sensitive by the use of the anion-exchange resin Dowex 1-X8 (limit of detection, 0·03 μg of In). One drop of the sample soln. is mixed with one drop each of satd. ammonium acetate soln., *N* aq. NH_3 and 0·01% **I**, and to the mixture are added 3 to 5 grains of the resin in acetate form (50 to 100 mesh). The colour develops after a time and becomes an intense purple within 10 hr. The sensitivity is also increased by the use of resin grains impregnated with the **I** soln. Interference is caused by ZrO^{2+}, UO_2^{2+}, AsO_3^{3-}, MoO_4^{2-}, WO_4^{2-}, Al^{3+} (all give a similar coloration), Sn^{2+} and Ge (orange coloration); Al (equiv. to <1000 times 0·3 μg of In) is masked with F^- (>300 μg). K. SAITO

1226. **Quantitative determination of thallium as the dichromate. I. Gravimetric and volumetric methods.** N. I. Bashilova (N. S. Kurnakov Inst. of Gen. and Inorg. Chem., Acad. of Sci., USSR, Moscow). *Zhur. Anal. Khim.*, 1958, **13** (5), 545–554.—The pptn. of Tl as $Tl_2Cr_2O_7$ from neutral and H_2SO_4 soln. by means of CrO_3 soln. is studied. The

method may be used for the volumetric determination of Tl by determining the excess of CrO_3 iodimetrically. As the acid concn. increases, the amount of CrO_3 required for complete pptn. of $Tl_2Cr_2O_7$ also increases. After mixing the reagents, the soln. and ppt. are allowed to stand overnight and the excess of CrO_3 is determined iodimetrically in an aliquot of the filtrate. For the purpose of developing a gravimetric method for determining Tl as $Tl_2Cr_2O_7$, it was established by phase differential thermal analysis that washing the ppt. with acetone or ethanol does not cause decomposition, while washing with water causes formation of the mono-chromate. To determine Tl gravimetrically, precipitate it from not more than 100 ml of soln. containing up to 10 g of H_2SO_4 with a soln. of CrO_3 so as to give a concn. of CrO_3 of between 1 and 2 g in 100 ml. Cool the ppt. and soln. to between 0° and 3° for 3 to 4 hr., filter, wash the ppt. with a cooled CrO_3 soln. of concn. the same as that of the original soln., then with a 0·25% soln. of CrO_3, and finally with acetone or ethanol till no more chromate appears in the wash liquor. Dry to const. wt. at 110° to 130° and weigh. C. D. KOPKIN

1227. **Determination of traces of thallium.** A. Radu. *Rev. Chim., Bucharest*, 1958, **9** (6), 326–328.—Thallium is determined by forming the complex with methyl violet, extracting with toluene and measuring the colour. Methods of eliminating interfering elements are given. H. SHER

1228. **Isolation of carrier-free yttrium by electrodeposition from a mixed radioactive system with strontium.** Hiroshi Hamaguchi, Nagao Ikeda and Toshi Kawashima (Fac. of Sci., Tokyo Univ. of Education, Koishikawa). *Japan Analyst*, 1958, **7** (4), 243–246.—Kruss's electrolytic deposition of Y on a copper cathode (*Z. anorg. Chem.*, 1893, **3**, 60) was applied to the separation of carrier-free ^{90}Y from ^{90}Sr. Radiochemically pure (>99·9%) ^{90}Y is deposited on copper (or platinum) from an ammonium nitrate or sulphate soln. (≃0·5 *M*) of pH 5 to 6 on application of 2 to 6 V. The ^{90}Y is readily dissolved with dil. mineral acids. K. SAITO

1229. **Solubility of yttrium oxalate.** A. M. Feibush, K. Rowley and L. Gordon (Dept. of Chem., Brookhaven Nat. Lab., Upton, L.I., N.Y.). *Anal. Chem.*, 1958, **30** (10), 1610–1612.—The solubility of Y oxalate is determined over a wide range of oxalate concn. within the pH range 0·5 to 4·6. The solubility product is $5{\cdot}34 \times 10^{-29}$. When the oxalate activity exceeds 10^{-3} *M* there is evidence of formation of a trioxalate complex. The dissociation constants are, for $Y(C_2O_4)^+$, $K_1 \simeq 3 \times 10^{-7}$; for $Y(C_2O_4)_2^-$, $K_2 \simeq 8 \times 10^{-11}$; and for $Y(C_2O_4)_3^{3-}$, $K_3 \simeq 3{\cdot}4 \times 10^{-12}$. T. R. ANDREW

1230. **Spectrophotometric determination of lanthanum in plutonium.** K. S. Bergstresser (Univ. of Calif., Los Alamos Scientific Lab., N.M., U.S.A.). *Anal. Chem.*, 1958, **30** (10), 1630–1632.—The plutonium is oxidised with $HClO_4$ and the lanthanum pptd. with HF. The ppt. is dissolved in fuming $HClO_4$ and the lanthanum is re-pptd. with 8-hydroxyquinoline. The lanthanum oxinate is dissolved in 0·1 *N* HCl and the extinction of this soln. is measured at 365 mμ. The standard deviation for a single measurement is equivalent to 3 μg for a range of 40 to 200 μg of lanthanum. K. A. PROCTOR

1231. **Determination of cerium with potassium periodate.** I. V. Puzdrenkova, I. P. Alimarin and V. A. Frolkina. *Vestn. Moskov. Univ.*, 1958, (2), 183–186.—It is shown that the ppt. of cerium periodate formed at pH 2 to 3 has the composition $CeHIO_6.3H_2O$ (air-dry) and may be dried at 120° to give the anhyd. salt, which does not begin to decompose below 200°. With 4 to 5 mg of Ce, complete pptn. is attained at pH 2 to 7. The temp. has no effect on the completeness of pptn. (high temp. give a readily collected ppt.), nor has the presence of SO_4^{2-}, NO_3^- or Cl^-. Completeness of pptn. was tested with the radioactive isotope ^{141}Ce, and it was found that the amount of Ce not pptd. is ⩾1·5%. If the Ce is present as Ce^{IV}, a threefold amount of reagent is necessary; if it is present as Ce^{III}, a fivefold amount is required. To determine 1 to 30 mg of Ce, add to the acid soln. (30 to 50 ml) a fivefold excess of reagent (a 1% soln. of KIO_4 in 1% KOH soln.). Add 2 *N* KOH dropwise to a pH of 2 to 3. Warm to obtain a flaky ppt., cool, and filter through a glass filter. Wash the ppt. with cold water to remove IO_4^-, dry to const. wt. at 120° to 130° and weigh as $CeHIO_6$. Alternatively, dissolve the washed ppt. in a small amount of conc. H_2SO_4, reduce the IO_4^- with H_2O_2 or iodide and boil out the liberated iodine. Cool, make up to 50 ml and determine Ce colorimetrically with 8-hydroxyquinoline. The presence of a 100-fold excess of La or Pr or both does not influence the determination. To determine Ce in monazite sand, decompose the sample on a sand bath with conc. H_2SO_4, remove the silica, separate Ce and Th with KIO_4, dissolve the ppt. in HCl, destroy the periodate with H_2O_2, boil out the iodine, and determine Ce in an aliquot of the soln. volumetrically with $(NH_4)_2SO_4.FeSO_4.6H_2O$ or colorimetrically with 8-hydroxyquinoline. C. D. KOPKIN

1232. **Photometric determination of cerium as cerium-molybdic heteropoly acid.** Z. F. Shakhova and S. A. Gavrilova (M. V. Lomonosov Moscow State Univ.). *Zhur. Anal. Khim.*, 1958, **13** (2), 211–214.—The method is based on the formation of the Ce - molybdic acid complex. It is found to be stable for 30 min. at an acidity of 0·1 to 0·3 *N* H_2SO_4 or 0·4 *N* $HClO_4$, and obeys Beer's law. Spectrophotometric measurement is carried out at 380 mμ. W. ROUBO

1233. **Polarography of europium and ytterbium.** J. O. Hibbits, M. R. Menke and W. F. Davis. *U.S. Atomic Energy Comm.*, Rep. APEX-405, 1958, 19 pp.—Most rare earths are reduced at approx. the same potential and interfere with each other. Europium and ytterbium are reduced at a more positive potential and do not influence each other or the other members of the group. Characteristics and data obtained when LiCl, NH_4Cl and tetramethylammonium bromide were used as electrolytes are recorded. S.C.I. ABSTR.

1234. **Separation of trace amounts of rare earths from various metals.** M. W. Lerner. *U.S. Atomic Energy Comm.*, Rep. NBL-143, 1958, 13–16.—Rare-earth metals are separated from zirconium, titanium, uranium ore and stainless steel. A pptn. as the fluoride is carried out with thorium as carrier in the presence of NH_4F. The separation is completed by dissolving the thorium and rare-earth fluorides in HNO_3, containing boric acid, and pptg. as the oxalate. The thorium is extracted with 8-hydroxyquinoline in $CHCl_3$. The rare-earth

metals are then pptd. as oxinates with added lanthanum as carrier, which also serves as an internal standard for subsequent spectrographic analysis. This procedure is applied to uranium samples dissolved in HNO_3 after the addition of HF. For stainless-steel samples dissolved in aqua regia, oxidation of CrF_3 with $HClO_4$ is necessary before pptn. of the fluorides. Bismuth must be removed as the oxychloride or by electrolysis with a mercury cathode before the oxalate pptn. A table of recoveries is given. K. R. C.

1235. **Procedure for pH control during the separation of rare earths by ion-exchange chromatography.** G. Brunisholz (Univ., Lausanne, Switzerland). *Chimia*, 1958, **12** (6), 180 (in French).—Elution of rare-earth metals from an ion-exchange column with EDTA (acid) is slow at a high pH, but at too low a pH pptn. of EDTA (acid) or of an acid salt may occur. A suitably low pH is maintained by the addition of ammonium acetate or formate to provide a buffer at $\simeq$pH 3 (yttrium earths) or $\simeq$pH 4 (cerite earths), respectively. A high final concn. of acetic or formic acids is avoided by using a soln. of EDTA (triammonium salt) as eluent. A preliminary titration of the eluent with $ZnSO_4$ and a mixed methyl red - methylene blue indicator is necessary to determine the available acidity, whence the required amount of ammonium acetate or formate can be calculated. J. H. Waton

1236. **Quantitative spectrographic analysis of rare-earth elements and thorium in their mixtures by solution method.** Lien-Fang Shen, Chien-Hwa Chen, Bun-Lee Huang and Ting-Chao Chang (Inst. of Appl. Chem., Acad. Sinica). *Acta Chim. Sinica*, 1958, **24** (4), 286–294.—The rare-earth elements and thorium are separated from minerals by chemical methods. The cerium oxide content is determined volumetrically and this is then raised to 80·0% by adding pure cerium compound (*cf.* Fassel, *Brit. Abstr. C*, 1950, **3**). A drop of the resulting chloride soln. is placed on the flat top of a graphite electrode, which has been previously treated with a drop of liq. paraffin. The electrode is dried and the sample is excited in a triggered a.c. arc. Spectral line-pairs for the determination of La, Nd, Sm, Pr, Y, Gd, Dy, Yb and Er have been selected in the region of 350 to 450 mμ, whereas that of Th falls in the u.v. region. Cerium is used as internal standard. The standard errors for the determination of 10 elements vary from 2·9 to 8·8%. It is claimed that the present method is free from line interference and systematic error. S. H. Yuen

1237. **Co-precipitation in some binary systems of rare-earth oxalates.** A. M. Feibush, K. Rowley and L. Gordon (Dept. of Chem., Brookhaven Nat. Lab., Upton, L.I., N.Y.). *Anal. Chem.*, 1958, **30** (10), 1605–1609.—The validity of the Doerner - Hoskins logarithmic distribution law is demonstrated for the Nd - Ce, Y - Ce, Yb - Ce and Yb - Nd systems. Radioactive tracers were used to establish relative concn. in the soln. and ppt. over the range of 0 to 100% of the host element pptd. The effect of varying the conditions of pptn. with dimethyl oxalate is studied. Calculations based on solubility products are shown to be invalid. T. R. Andrew

1238. **Determination of rare-earth elements in minerals and concentrates by X-ray fluorescence analysis.** R. L. Barinskiĭ. *Zavod. Lab.*, 1958, **24** (5), 613–617.—A stabilised power source, a tube with a tungsten target working at 25 kV and 15 mA, a curved quartz crystal (50 cm radius) and an evacuated spectrometer are used for determining La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu in samples (10 to 20 mg) which are applied uniformly to the surface of aluminium discs (15 to 17 mm in diam.) giving a thickness of $<$0·05 mm. For all the elements except Eu, Gd and Tm, the L_{α_1} and L_{β_1} lines, which are not subject to interference, are measured. For Eu, Gd and Tm a difference method is used, based on the fact that the lines Eu L_{β_1}, Gd L_{β_1} and Tm L_{α_1} are exactly superimposed on the lines Dy L_{α_2}, Ho L_{α_1} and Sm L_{γ_1}, the intensities of which are found from analysis of pure materials to bear the ratios 0·12, 1·9 and 0·1 to the intensities of the lines Dy L_{α_1}, Ho L_{β_1} and Sm L_{β_1} which are not subject to interference. The range of the method is 0·1 to 100% and the highest accuracy (2 to 5%) is attained with concn. $<$1 to 3%. G. S. Smith

1239. **Gas-volumetric determination of carbon dioxide.** R. Engst (Inst. f. Lebensmittelchemie beim Magistrat von Grosz-Berlin). *Z. Lebensmitt-Untersuch.*, 1958, **107** (1), 32–40.—Three methods, *viz*, Tillmans', Rauscher's and Schmitt's, with accuracies of $\pm$3, $\pm$2 and $\pm$4%, respectively, are compared. Sources of error in assessing the gas vol. are discussed. A proposed modification of Rauscher's method (*Pharm. Zentralh.*, 1947, **86**, 361) is described and a diagram of the burette is given, together with data of a test analysis. Data on 20 analyses of $NaHCO_3$ (99·95%) are given. Apart from weighing, the test takes $>$2 min. and experimental error is within $\pm$0·5%. The method is suitable for routine analysis. S.C.I. Abstr.

1240. **Conductimetric determination of [total] carbonates and bicarbonates when present together.** G. B. Pasovskaya (Turkmen Med. Inst., Ashkhabad). *Zhur. Anal. Khim.*, 1958, **13** (5), 619–621.—Total carbonates and bicarbonates are determined by adding excess of HCl (0·01 *N*) (5 ml) and acetic acid (0·01 *N*) (5 ml), diluting to 25 ml, and titrating the excess of HCl conductimetrically with 0·1 *N* $Ba(OH)_2$. The sharp angle in the titration curve indicates the end-point. Down to 0·002 milliequiv. may be determined in 25 ml. No interference is caused by Ca, Mg or NH_4^+. Iron may be masked with NaF. To eliminate the influence of SO_4^{2-}, add a little solid $BaSO_4$ and a soln. of methyl violet, and a small vol. (0·5 to 2 ml, depending on the amount of SO_4^{2-}) of a 1% soln. of $BaCl_2$. Phosphates interfere, but may be removed by adding 5 ml of the 1% soln. of $BaCl_2$ and filtering after 1 or 2 min. After washing the ppt., the combined filtrate and wash liquor is treated as above and titrated. The method may be used to determine the hardness of water. C. D. Kopkin

1241. **Radiochemical analysis of silicon.** J. A. James and D. H. Richards. *J. Electronics and Control*, 1957, **3**, 500–506.—Results of radioactivation analyses for some 12 elements are given for silicon from two sources. The results of segregation coefficient measurements using radiochemical methods are quoted for P, Fe, Co, W and Au. Phys. Abstr.

1242. **Volumetric determination of silica in quartz and silicon carbide.** F. Heltai and E. Beke. *Rev. Chim., Bucharest*, 1958, **9** (6), 311.—The method is based on the formation of K_2SiF_6, its hydrolysis in

boiling water and titration of HF liberated with NaOH. *Procedure*—The sample (≃1 g) is heated in a platinum crucible with 5 to 6 g of a mixture of K_2CO_3 (85 to 90%) and boric acid (10 to 15%) until the mass is melted and evolution of CO_2 begins. The melt is dissolved in H_2O, the crucible and lid are washed with conc. HCl and the soln. is acidified with conc. HCl and made up to 1 litre. A 100-ml aliquot is treated with 8 to 10 ml of conc. HCl and boiled for 2 to 3 min. The soln. is cooled to between 30° and 40°, poured into a plastic beaker, and treated with 1 g of NaF, stirred and saturated with KCl. The ppt. is washed until neutral with a soln. of 7 g of KCl in 100 ml of 50% ethanol. The ppt. is washed into a flask with 400 to 500 ml of boiling H_2O and titrated with NaOH soln. to phenolphthalein. It is claimed that the whole determination requires only 90 min. and that the accuracy is satisfactory. H. SHER

1243. **Sensitive detection of lead and the incorporation of lead in zinc sulphide.** E. A. Schwager and A. Fischer. *Z. Phys.*, 1957, **149** (3), 347–352.—Lead can be detected to 5×10^{-6} g of Pb per ml of solution by its characteristic luminescence in ZnS. In the presence of S vacancies, lead enters the ZnS lattice, giving a green emission; electrophotoluminescence occurs under u.v. With excess of S, mixed crystals of ZnS - PbS are formed, and a yellow emission is obtained which shifts to the red at low temperatures. PHYS. ABSTR.

1244. **Improvements in the determination of lead in lead concentrates.** S. D. Gur'ev, L. B. Zaĭchikova, V. P. Ioffe, N. F. Saraeva and N. N. Lutchenko. *Sb. Nauch. Trud. Gos. Nauch.-Issled. Inst. Tsvet. Met.*, 1958, (14), 9–20; *Ref. Zhur., Khim.*, 1958, (19), Abstr. No. 64,198.—The molybdate and two variations of the chromate (nitric acid and barium chromate) volumetric methods for the determination of Pb are examined. The influence of Ba [present as $Ba(OH)_2$] and Ca on the determination of Pb is studied. It is established that, in the pptn. of 100 to 200 mg of Pb, the presence of up to 2% of Ba [3% of $Ba(OH)_2$] and up to 75 mg of Ca does not influence the accuracy of determining Pb by the molybdate method; with larger amounts of Ba and Ca the results obtained are low and high, respectively. The presence of up to 50 mg of quartz or up to 100 ml of gelatinous SiO_2 does not cause interference. The presence of 6 to 9 mg of SO_4^{2-} (2 to 3% on a sample of 0·3 g) has no influence on the results of the chromate method. The possibility is shown of removing the influence of SO_4^{2-} by adding Ba; with a content of Pb of 100 to 200 mg, the addition of 0·5 g of $BaCl_2.2H_2O$ when decomposing the sample removes the influence of 30 to 45 mg of SO_4^{2-} (10 to 15% on a sample of 0·3 g). With a content of $SO_4^{2-} > 15\%$, this method is not satisfactory and low results are obtained for Pb. The nitric acid variation of the chromate method for determining Pb may be used for the analysis of concentrates containing up to 15% of SiO_2, 8% of As and 3% of SO_4^{2-}. With a content of 3 to 15% of SO_4^{2-}, the barium chromate variation is used. Both the molybdate and chromate methods give reproducible results with a relative error of from ±0·2 to ±1% with a content of 20 to 75% of Pb. C. D. KOPKIN

1245. **Use of polarography in the phase analysis of lead compounds in ores and their enrichment products.** N. I. Solntsev and R. I. Chudina. *Sb. Nauch. Trud. Gos. Nauch.-Issled. Inst. Tsvet. Met.*, 1958, (14), 80–92; *Ref. Zhur., Khim.*, 1958, (19), Abstr. No. 64,199.—A procedure is described for the polarographic determination of all forms of Pb. The following list gives the composition of the solvents used for dissolving the separate forms of Pb, with the composition of the basal soln. for the polarographic determination of Pb in brackets. Total Pb—10 ml of HCl, sp. gr. 1·19 for 0·5 to 1 g of ore (0·5 ml of a 5% soln. of $FeCl_3$ and 99·5 ml of HCl, 1:3); Pb of anglesite—100 ml of 4·3 *M* NaCl for 1 to 2 g of ore (10 g of NaCl, 10 ml of HCl, sp. gr. 1·19, and water to 100 ml); Pb of cerussite—100 ml of 2 *M* ammonium acetate containing 2% of acetic acid on the preceding residue (12 g of ammonium acetate, 2 ml of 80% acetic acid, and water to 100 ml); Pb of crocoisite and wulfenite—100 ml of 0·5 *M* NaOH and 50 ml of 0·6 *M* ammonium acetate (successively) on the preceding residue (2 g of NaOH, 1 g of ammonium acetate, and 100 ml of water for wulfenite; 0·8 g of NaOH and water to 100 ml for crocoisite; 20 g of NaOH, 2 g of ammonium acetate, 0·5 g of Na_2SO_3, and water to 100 ml, or 0·05 g of ascorbic acid, 2 g of NaOH, and water to 100 ml for wulfenite and crocoisite); Pb of pyromorphite and vanadinite—100 ml of 4·3 *M* NaCl acidified with HCl on the preceding residue (10 g of NaCl, 2 g of NaOH, and water to 100 ml); Pb of pyromorphite, mimetite, crocoisite and wulfenite—100 ml of 4·3 *M* NaCl acidified with HCl on the residue after solution of cerussite (10 g of NaCl, 0·5 ml of a 5% soln. of $FeCl_3$, 9 ml of HCl, sp. gr. 1·19, and water to 100 ml for pyromorphite, mimetite, crocoisite and wulfenite; 10 g of NaCl, 2 g of NaOH, and water to 100 ml for vanadinite, pyromorphite and mimetite; 20 g of NaOH, 2 g of ammonium acetate, 0·5 g of Na_2SO_3, and water to 100 ml, or 0·05 g of ascorbic acid, 2 g of NaOH, and water to 100 ml for crocoisite, vanadinite, pyromorphite and mimetite); Pb of galena—100 ml of 4·3 *M* NaCl containing 0·2 *M* $FeCl_3$ on the residue after extraction with acid 4·3 *M* NaCl (10 g of NaCl, 24 g of $FeCl_3$, 10 ml of HCl, sp. gr. 1·19, and water to 100 ml); Pb of beaverite, beudandite and plumbojarosite—dry the preceding residue, ash and ignite in a porcelain crucible at 400° to 500° and dissolve in 10 ml of HCl, sp. gr. 1·19 (0·5 ml of a 5% soln. of $FeCl_3$ and 99·5 ml of HCl, 1:3). The procedure described gives satisfactorily accurate results and takes about half the time of the chemical analysis. C. D. KOPKIN

1246. **Rapid determination of small amounts of lead in electrolytic manganese and ferromanganese.** Hidehiro Gotó and Kichinosuke Hirokawa. *Sci. Rep. Res. Inst. Tohoku Univ.*, 1958, **10**, 10–19.—Spectrophotometric determinations of Pb in electrolytic manganese and ferromanganese with the dithizone method were investigated. Lead in electrolytic manganese was determined by dithizone extraction with ammonium citrate as a masking reagent for large amounts of Mn, and KCN as a masking reagent for other heavy metals. With ferromanganese, the Pb in the sample was separated from Fe and Mn by dithizone extraction, the Pb dithizonate was shaken with diluted HNO_3 to transfer the Pb to the aq. phase, and the Pb was then determined by the dithizone method. These methods were applied to 0·002 to 0·05% of Pb in electrolytic manganese and ferromanganese, and satisfactory results were obtained. The time required for these procedures was 25 to 40 min. for one sample. CHEM. ABSTR.

1247. **Studies on organic reagents for inorganic analysis. III. Colorimetric determination of titanium with phenylfluorone.** Hirotoshi Sano (Chem. Dept., Fac. of Sci., Tokyo Univ., Hongo, Tokyo). *Japan Analyst*, 1958, **7** (4), 235–238.—Like Ge, Sn and Zr, Ti^{IV} produces an orange complex (max. absorption, 525 mμ) with phenylfluorone in an acid soln., which obeys Beer's law for $<2{\cdot}5$ p.p.m. of Ti. The sensitivity is 20 times as great as that of the peroxide or the alizarin red S method. The complex is soluble in 0·1 *N* HCl soln. containing 5 ml of *cyclo*hexanol and 20 ml of ethanol per 50 ml. Serious interference results from Fe^{III}, Ge, Sn^{IV}, Zr and Sb^{III}. K. Saito

1248. **Determination of bi- and ter-valent titanium in slags containing metallic and bivalent iron.** L. I. Veselago (A. A. Baĭkov Inst. of Metall., Acad. Sci., USSR, Moscow). *Zhur. Anal. Khim.*, 1958, **13** (5), 562–566.—Take 0·2 to 0·5 g of slag, add H_3PO_4 (sp. gr. 1·7) (25 to 35 ml), pass CO_2 through the flask for 15 min., and decompose the sample by warming for 20 to 30 min. with constant stirring. Cool, add H_2SO_4 (1:4) (50 ml) and cool to room temp. in an atm. of CO_2. Cut off the flow of gas, add a 40% aq. soln. of NH_4SCN (20 ml) and titrate with 0·05 *N* $(NH_4)_2SO_4.(Fe)_2(SO_4)_3$ till the colour of the soln. changes from yellow to orange (titre V_1). This represents total Ti^{III}, made up of Ti^{III} originally present and that obtained by oxidation of Ti^{II} during the treatment with H_3PO_4. As an alternative procedure, take 0·2 to 0·5 g of slag, add a 10% aq. soln. of $CuSO_4$ (15 ml), dilute to 50 ml and boil for 15 to 20 min. in a stream of CO_2 to dissolve metallic Fe. Filter, and wash the residue with hot water. To the filtrate add H_2SO_4 (1:3) (20 ml), H_3PO_4 (sp. gr. 1·7) (15 ml) and dilute to 150 or 200 ml; titrate with 0·01 *N* ammonium vanadate with barium diphenylaminesulphonate as indicator, thus determining metallic Fe. Treat the filter and the ppt. for 5 min. in the cold with a HCl soln. of $FeCl_3$ to dissolve metallic Cu. Filter, wash with hot water and then several times with cold 5% H_2SO_4. Wash the ppt. from the filter with a stream of hot water, add excess of $(NH_4)_2SO_4.Fe_2(SO_4)_3$ soln. and 5 ml of H_2SO_4 (sp. gr. 1·84), and pass CO_2 for 15 min. Add HF (10 ml) (total vol. should be $\simeq$50 ml), stir and heat for 20 or 30 min. to complete decomposition of the slag. Cool in a current of CO_2, add a saturated boric acid soln. (20 ml) to take up the F^-, transfer the soln. to a flask containing 30 to 50 ml of water and 5 ml of conc. H_2SO_4, and titrate Fe^{2+} (equiv. to total Ti^{II} and Ti^{III}) with 0·05 *N* $KMnO_4$ (titre V_2). The correction for the presence of Fe^{II} in the slag is obtained as follows. Treat 0·5 g of slag as described above to remove metallic Fe. Decompose the slag in a current of CO_2 by heating with a mixture of 5 ml of conc. H_2SO_4 and 10 ml of HF and dilute to 50 ml. Transfer the soln. to a flask containing 20 ml of saturated boric acid soln., 5 ml of conc. H_2SO_4 and 15 ml of conc. H_3PO_4; the total vol. should be 150 to 200 ml. Add 1 ml of a 5% aq. soln. of sodium tungstate and titrate residual Ti^{II}, not oxidised during the HF decomposition, with $KMnO_4$ soln. Then titrate Fe^{2+} in the same soln. with 0·01 *N* ammonium vanadate, with barium diphenylaminesulphonate as indicator (titre V_3). Then the actual quantity of $KMnO_4$ used for the titration of the Fe^{2+} equiv. to total Ti^{II} and Ti^{III} is $V_2 - V_3 = V_0$. Convert the titres of the $(NH_4)_2SO_4.Fe_2(SO_4)_3$, $KMnO_4$ and ammonium vanadate soln. used in the titrations to a single normality and a single wt. of sample. Then—

$$TiO\,(\%) = \frac{63{\cdot}9 \times N \times (V_0 - V_1) \times 100}{1000 \times n}$$

and

$$Ti_2O_3\,(\%) = \frac{143{\cdot}8 \times N \times (2V_1 - V_0) \times 100}{2 \times 1000 \times n},$$

where N is the standard normality and n is the standard wt. of sample. Reproducible results are obtained, with relative accuracy of 0·5 to 1·0% for 10 to 60% of Ti and 6% for 1 to 5% of Ti.

C. D. Kopkin

1249. **Determination of tervalent titanium with sulphosalicylic acid in the presence of iron and other elements.** V. M. Peshkova and Kim Khen Rak. *Vestn. Moskov. Univ.*, 1958, (2), 187–195.—To determine Ti in pure soln., take 5 ml of soln. in a separating funnel, add 5 ml of *N* HCl and a little liquid zinc amalgam, saturate the soln. with CO_2 and shake for 2 to 3 min. Separate the amalgam, transfer the soln. to a 50-ml flask filled with CO_2, rinsing the funnel with water, add to the flask 8 ml of a 10% soln. of sulphosalicylic acid (**I**) and 10 ml of a 10% soln. of Na acetate neutralised with aq. NH_3 to pH 4·5 to 7, make up to vol. and measure the extinction at 461 mμ, on a spectrophotometer. All reagents are stored in an atmosphere of CO_2. To determine Ti in the presence of Fe, to the soln. containing 0·05 to 14 mg of Ti add 10% aq. NH_3 dropwise, carefully and with stirring, till $Fe(OH)_3$ just forms, add 2 to 2·5 ml of conc. HCl, and make up to 50 ml. Reduce 10 ml of the soln. and determine Ti as described above. The presence of a drop of amalgam in the colorimeter cell does not affect the measurement, and by shaking the soln. just before measuring the extinction, air oxidation of Ti is avoided. The blank soln. should contain the same concn. of Fe as the analytical soln., and is treated analogously. No interference is caused by Mn, Ca or Mg; Al forms with **I** a colourless complex which does not absorb at 460 to 462 mμ, an additional 10 ml of the soln. of **I** being used for each mg of Al present; Cu^{II} is reduced to metal and in small amounts does not interfere; larger amounts of metallic Cu are filtered off; Nb and Ni do not form coloured complexes with **I**; the influence of the colour of Ni^{2+} is removed by adding an equal amount of Ni^{2+} to the blank; Mo^{III} and V^{III} form coloured complexes with **I** but, in the presence of Cr^{II} or Nb^{III} and with zinc amalgam as reducing agent, V^{III} is reduced to V^{II} and does not interfere. In the presence of Mo and large amounts of Cr^{II}, similar amounts are added to the blank soln., and the quantity of **I** soln. used is increased by 1 ml for each mg of Mo and Cr. To determine Ti in iron ores, dissolve 0·2 g of ore in 3 ml of conc. HCl in a small beaker, add 10 ml of hot water and, in small portions, 10% aq. NH_3 until a slight permanent ppt. is formed. Add 2 to 2·5 ml of conc. HCl, filter and wash into a 50-ml flask, and make up to vol. Determine Ti as described above in 10 ml of the resulting soln. To determine Ti in acid- and heat-resistant steel, dissolve 0·2 g of steel in 3 ml of a mixture (1:1) of conc. HCl and HNO_3. Add 1 to 2 ml of conc. H_2SO_4 and evaporate on a sand bath to remove HNO_3 completely. Dilute to 20 ml and determine Ti as described above, introducing Cr and Ni into the blank soln. in amounts corresponding to their concn. in the analytical soln. The analysis takes <1 hr. and 0·6 μg of Ti per ml can be determined in the presence of 10^4 times the amount of Fe with satisfactory accuracy (*e.g.*, within $\pm$5% at a ratio of Ti to Fe of up to 1 to

1000). The coloured soln. obey Beer's law. At pH 4·4 to 5·5 the absorption curves of the complexes of **I** with Ti^{III} and/or Ti^{IV} show an isosbestic point, *i.e.*, the curves cross, at 460 to 462 mμ, so that any partial oxidation of Ti^{III} does not affect the extinction. In this pH interval the relative error of the determination of Ti in pure soln. is ≯5%; in the pH range 4·8 to 5·3 the error is ≯1%. The extinction may also be measured on a photo-electric colorimeter at 455 mμ, which, however, is not the isosbestic point. C. D. KOPKIN

1250. **Simultaneous estimation of titanium and iron in silicates by polarographic method.** S. Kumar and B. C. Sinka (Centr. Glass & Ceram. Res. Inst., Calcutta). *Bull. Centr. Glass Ceram. Res. Inst.*, 1958, **5** (1), 18–24.—Quadrivalent Ti and Fe^{3+} give well-developed $E_{\frac{1}{2}}$ values of −0·18 and −0·55 V, respectively, at pH 1·3 (adjust with H_2SO_4) in a supporting electrolyte of 0·1 *N* $Na_4P_2O_7.10H_2O$ (11·2 g per 100 ml) containing 0·005% of gelatin, and after N has been bubbled through to remove the O. The sample is decomposed with HF - H_2SO_4 and a few drops of HNO_3 or by fusion with Na_2CO_3 - $Na_2B_4O_7$. Phosphates, sulphates and Sb_2O_3 do not interfere, but Cl^- must be removed. The presence of Mn^{3+} may cause interference with the determination of Fe^{3+}, and the sample is then decomposed with HF - H_2SO_4 - H_2O_2 in order to oxidise the Fe^{2+} and to reduce the Mn^{3+} to Mn^{2+}. The excess of H_2O_2 and a yellow colour (probably due to Ti) are removed by boiling the soln. The sensitivity of the method is 10 p.p.m. of Ti. J. A. SUGDEN

1251. **Analytical methods for the determination of titanium and iron in titaniferous clays.** J. Gottfried (Res. Inst. Inorg. Chem., Ústí nad Labem, Czechoslovakia). *Chem. Průmysl*, 1958, **8** (4), 176–180.—Various methods were studied and the described procedures were tested by analysing thousands of clay samples as well as products and intermediates of their chemical conversion into $TiCl_3$. *Potentiometric method*—The sample after the removal of silicic acid is fused with $KHSO_4$, dissolved in H_2SO_4 (1 + 3), oxidised with a small excess of 0·1 *N* $KMnO_4$, and titrated with 0·1 *N* $CrSO_4$ in an inert atmosphere (CO_2). In the presence of Fe, two distinct changes of potential appear. *Colorimetric method with chromotropic acid*—The sample (0·1 g) is ignited, SiO_2 is removed, the residue is fused with $KHSO_4$, dissolved in H_2SO_4 (1 + 1) (3 ml) and H_2O (10 ml) and transferred to a 500-ml flask. To 5 ml of this soln. in a 50-ml flask are added $CuSO_4$ soln. (10%) (10 ml), Na formate (23 g of formic acid and 4 g of NaOH in 1 litre of H_2O) (10 ml) and chromotropic acid soln. (3%) (2 ml). The mixture is diluted to vol. and the extinction measured with an S47 blue filter. *Rapid method with H_2O_2*—The calcined sample (0·1 g) is fused with $KHSO_4$ in a porcelain crucible, the melt is dissolved in a mixture of H_2SO_4 (5%) and H_2O_2 (5%) and the yellow colour is compared with a standard in a 100-ml cylinder. J. ZÝKA

1252. **Determination of carbon in titanium, zirconium and their alloys by gravimetric and conductimetric methods.** D. F. Wood and M. Williams (Imperial Chemical Industries, Ltd., Kynoch Works, Birmingham). *Metallurgia, Manchr*, 1958, **58**, 47–52.—The merits of various fluxes and the advantage of using argon to moderate the oxidation of Ti and Zr are discussed. A detailed description of the procedure for both methods is included. It is concluded that carbon can satisfactorily be determined in titanium and zirconium and their alloys by both methods by the use of argon. A Bi - Fe flux is recommended for zirconium whilst lead is necessary for titanium. A precision of ±0·005% and ±0·001% for the gravimetric and conductimetric methods, respectively, is claimed. J. W. O. PYEMONT

1253. **Flavianic acid, a new selective reagent for zirconium.** T. Naşcaţiu and G. Baiulescu (Lab. Phys. Chem. Anal., Acad. R.P.R.). *Acad. R.P.R., Stud. Cercet. Chim.*, 1958, **6** (1), 31–35.—The reagent flavianic acid (2:4-dinitro-1-naphthol-7-sulphonic acid) (**I**) gives a ppt. with Zr in acid soln. to the exclusion of 50 other elements; only F^-, SO_4^{2-}, tartrate and citrate interfere. *Procedure*—The soln. of Zr^{2+} in a vol. of 80 to 100 ml is treated with a conc. soln. of **I** and ≃5 ml of conc. HCl (the ppt. is stable in 7·5 *N* HCl) until all the Zr is pptd. The mixture is boiled, filtered quickly and the ppt. washed with a boiling soln. (0·2%) of **I**. The ppt. is calcined to ZrO_2, care being taken to moisten it on the filter-paper with a little H_2SO_4 to avoid loss by crepitation due to the nitro groups in the reagent. H. SHER

1254. **Spectrophotometric determination of thorium with 2-(4-carboxy-3-hydroxyphenylazo)-1:8-dihydroxynaphthalene-3:6-disulphonic acid.** Sachindra Kumar Datta (Chem. Lab., Darjeeling Gov. Coll., India). *Anal. Chem.*, 1958, **30** (10), 1653–1656.—2-(4-Carboxy-3-hydroxyphenylazo)-1:8-dihydroxynaphthalene-3:6-disulphonic acid (**I**), prepared by coupling chromotropic acid with diazotised 4-aminosalicylic acid, reacts with Th^{4+} in weakly acid soln. to give a soluble red - violet complex with an absorption max. at 580 mμ. Within the pH range 2·5 to 3·5, (**I**) may be employed for the quant. determination of Th. The colour is stable for 24 hr., and the complex is unaffected by heat up to 60°. Of 17 ions studied, only Fe^{3+}, Ce^{4+}, Zr^{4+}, Au^{3+}, PO_4^{3-} and F^- interfere seriously. Suitable conditions are 0·1 to 1·0 mg of Th, 1 ml of 0·1% **I** soln., a pH of 2·5, and a final vol. of 25 ml. Mix well, and measure the extinction at 580 mμ against a reagent blank. The procedure has been applied to monazite sands. T. R. ANDREW

1255. **Photometric determination of thorium with arsenazo in the presence of zirconium, titanium and rare earths.** F. V. Zaĭkovskiĭ and L. I. Gerkhardt (All-Union Inst. Min. Raw Materials, Moscow). *Zhur. Anal. Khim.*, 1958, **13** (3), 274–279.—The interference of Zr^{4+}, Ti^{4+} and the rare-earth elements can be removed by means of tartaric acid. In the presence of large amounts of Ti^{4+} (8 μg per ml) a mixture of tartaric and ascorbic acids has been found better than tartaric acid alone. The extinction depends on pH and it has been found that the range of 1·3 to 3·0 is the best, giving a maximum absorption of the coloured complex. W. ROUBO

1256. **Synthetic and analytical studies on colour reagents. VII. Behaviour of o-arsono-o′-hydroxyazo compounds towards thorium, uranyl and lanthanum ions.** Koichi Emi, Kyoji Tôei and Kiyoshi Furukawa (Fac. of Sci., Okayama Univ., Tsushima). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1958, **79** (6), 681–686.—*o*-Aminobenzenearsonic acid (**I**), 2-amino-4-chlorobenzenearsonic acid and 2-aminonaphthalene-1-arsonic acid (**II**) were coupled with various coupling components and their colour reactions with Th, ZrO^{2+}, Ti, La, Sm, Al and UO_2^{2+}

were examined at various pH values. The optimum pH values for the reaction with these metals (1, 1, 4, 8, 8, 5 and 8, respectively, for the above-mentioned metals in the order given) are almost independent of the kind of reagent in this series. The coupling product of **II** and R-acid is most sensitive to these metals, the sensitivity being comparable with that of neothorin (product of **I** and chromotropic acid). K. SAITO

1257. **Gravimetric determination of thorium and zirconium. Quinaldic acid as a reagent.** A. K. Majumdar and J. G. Sen Gupta (Jadavpur Univ., Calcutta, India). *Z. anal. Chem.*, 1958, **162** (4), 262–265 (in English).—A study was made of the effect of various pH values on the quant. pptn. of Zr and Th as the quinaldates. It was found that Th was completely pptd. at pH 2·8 and Zr at pH 3. The ppt. were then ignited to their oxides as the original ppt. were non-stoicheiometric. Under the conditions described, Th was completely separated from As^{3+}, Hg^{2+}, Mg, Mn, alkaline earths and rare earths, while Zr was only slightly contaminated with rare-earth metals. S. BAAR

1258. **Volumetric determination of thorium in uranium alloys.** H. H. Willard, A. W. Mosen and R. D. Gardner (Univ. of California, Los Alamos Sci. Lab., N.M., U.S.A.). *Anal. Chem.*, 1958, **30** (10), 1614–1616.—Thorium is determined within the range 0·1 to 3% in U - Th, U - W - Th and U - Ti - Th alloys by pptn. as fluoride, with La as carrier, ignition to oxide, dissolution in HNO_3 and $HClO_4$, and, after adjustment to pH 2, titration with EDTA (disodium salt) soln. *Procedure*—For U - Th and U - Ti - Th alloys, dissolve the sample ($\simeq$10 mg of Th) in HCl, adding H_2O_2 to aid dissolution. Dilute to 25 ml and add $La(NO_3)_3$ soln. (5 ml containing 2 mg of La^{3+} per ml). Adjust the pH to between 2 and 3 with aq. NH_3 and transfer the soln. to a polyethylene beaker. Add a little filter-paper pulp, HF (5 ml of 48%) and NH_4F soln. (20 ml of 10%). Set aside for $\lt$ 2 hr. and filter through a No. 42 paper, with a plastic funnel. Wash with dilute HF (5% v/v of 48% HF) and ignite in platinum at 800°. Wash the oxides into the original (glass) beaker and rinse the crucible with HNO_3. Add HNO_3 (15 to 20 ml) and warm to dissolve the ppt., adding a few drops of HF to assist dissolution. Add $HClO_4$ (1 ml) and evaporate the soln. until a moist residue remains. Take up in H_2O (20 to 25 ml) and adjust the pH to 2·0 to 2·5 with HCl or NaOH. Titrate with 0·025 *M* EDTA (disodium salt), with Eriochrome cyanine RC as indicator. For samples containing W, it is essential that F be added before WO_3 pptn. as this carries down $\simeq$25% of the Th present. Dissolve the sample in a known vol. of HCl and H_2O_2 (5 ml). Transfer the soln. to a polyethylene beaker and add HF and NH_4F soln. as described above. Add an amount of aq. NH_3 calculated to adjust the pH to simulate the conditions in the preceding method. (This can best be done by carrying a sample through the first procedure and recording the amount of aq. NH_3 required.) Add $La(NO_3)_3$ soln. (5 ml) and complete the determination as before. A relative standard deviation of 0·56% is reported for 161 samples. T. R. ANDREW

1259. **Separation of thorium from rare earths by means of pyridine and its nitrate.** E. A. Ostroumov. *Zhur. Anal. Khim.*, 1958, **13** (2), 201–204.—A method for a quant. separation of thorium by means of a mixture of pyridine and its nitrate at pH 4·1 to 4·2 has been described. No pptn. occurs with Y, La, Ce^{III}, Nd, Pr, Er, Sm or Yb. The separation of thorium is complete and there is no need for re-precipitation. The reagent is prepared as follows —to 20 ml of distilled HNO_3 (sp. gr. 1·32 to 1·33) add an approx. equal volume of water and 34 ml of pyridine, and dilute to 100 ml with water. W. ROUBO

1260. **Separation of thorium from titanium, zirconium and other accompanying elements by homogeneous precipitation.** F. V. Zalkovskiĭ and L. I. Gerkhardt (All-Union Inst. of Mineral Raw Materials, Moscow). *Zhur. Anal. Khim.*, 1958, **13** (5), 513–518.—The pptn. of Th as oxalate with dioxalylacetone was studied. It was established that Th is quant. pptd. at pH 0·6 to 1·5 in the presence of Ca^{2+} as co-pptg. ions. Zirconium and Ti are sometimes pptd. in amounts up to 50 μg, but these quantities do not interfere in the determination of Th with arsenazo in the presence of tartaric acid. The rare-earth elements are also pptd., but do not interfere in the determination of Th. Heat to $\simeq$ 550° in a 10-ml porcelain crucible 0·5 g of dry Na_2O_2, 5 or 6 mg of Fe_2O_3, the sample (0·025 to 0·25 g), and 2·5 to 4 g of Na_2O_2. Cool and extract the melt with warm water. Filter, wash the hydroxide ppt. on the filter 2 or 3 times with a 0·5% soln. of NaOH and dissolve it in 20 to 30 ml of hot 5% (v/v) HCl. Add a saturated soln. of Na acetate neutralised to Congo red (pH $\simeq$5), dilute to 100 ml, add 1 ml of a 25% soln. of $CaCl_2$ and 15 ml of a soln. of dioxalylacetone. Boil for 15 or 20 min., dilute to 100 ml and allow to stand overnight. Filter, wash the ppt. 4 to 6 times with a 1% soln. of oxalic acid, transfer to a porcelain crucible, dry and ignite at 600° to 700°. Transfer the residue to a 50-ml beaker, add a few drops of water and 4 or 5 ml of conc. HCl, and evaporate twice to dryness with HCl. Dissolve the residue in 8 or 10 ml of water, add aq. NH_3 to pH $\simeq$3 (Congo red), 2 drops of HCl (sp. gr. 1·12) and 0·5 ml of a 1% soln. of ascorbic acid, and make up to 25 ml with 0·09 *N* HCl. To determine Th, take a 2 to 20-ml aliquot, add 0·5 ml of a 10% soln. of tartaric acid and 3 ml of a 0·05% soln. of arsenazo, make up to 25 ml with 0·09 *N* HCl and measure the extinction at 570 mμ with a yellow - green filter. Construct a calibration curve for the range 5 μg to 70 μg of Th in 25 ml of soln. The method determines 0·002 to 3·0% of Th in ores with satisfactory accuracy and reproducibility. The dioxalylacetone reagent is prepared by drying oxalic acid (150 to 200 g) at 90° to 100° for 4 hr., powdering it and continuing the drying for 1·5 hr.; dissolve 40 g of the dried acid in 100 ml of anhydrous acetone. Use the soln. on the following day. C. D. KOPKIN

1261. **The formol titration of ammonium salts.** J.-M. Bloch and J.-C. Gaschard. *Compt. Rend.*, 1958, **246** (8), 1219–1222.—In the usual formol titration there is a systematic error of $\simeq -3\%$. Whatever indicator is used for the initial neutralisation of the NH_4Cl, the pH obtained after the addition of excess of formaldehyde soln. (neutralised to phenolphthalein) is 3·5 to 5. This is appreciably more alkaline than that of a soln. of hexamine hydrochloride (pH 3·2). It is recommended that the titration is carried out in a water - ethanol - ether (1:2:1) medium with ethanolic NaOH and phenol red as indicator. The mean error for 0·1 *N* to 0·05 *N* soln. is 0·6% and for 0·01 *N* soln. 2 to 3%. E. G. CUMMINS

1262. **Microcrystalloscopic reaction for nitrate ion with 4-piperidino-1-phenylbut-2-ene.** A. S. Babenko and A. V. Dombrovskiĭ. *Ukr. Khim. Zhur.*, 1958, **24** (1), 99–102; *Ref. Zhur., Khim.*, 1958, (19), Abstr. No. 64,217.—4-Piperidino-1-phenylbut-2-ene (**I**) forms with NO_3^-, I^-, SCN^- and $Fe(CN)_6^{3-}$ poorly soluble crystals in the form of many-rayed stars or rosettes of straight needles. To detect NO_3^-, mix 1 drop of soln. on a watch-glass with 1 drop of a 10% soln. of **I** in 60% acetic acid and observe the crystals which form. To detect NO_3^- in the presence of SCN^-, I^-, $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$, to 1 drop of soln. add 1 or 2 drops of a saturated soln. of Ag acetate, centrifuge off the ppt. and continue as described above. Of the most common ions only the following interfere—$Cr_2O_7^{2-}$, MnO_4^-, I^-, SCN^-, $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$. The detectable minimum of NO_3^- is 0·6 μg, at a limiting dilution of 1 in 1670. **I** may also be used to detect SCN^-, I^- and $Fe(CN)_6^{3-}$ with detectable minima and limiting dilutions, respectively, of 0·4 μg (1 in $2{\cdot}5 \times 10^3$), 0·1 μg (1 in 1×10^4) and 0·1 μg (1 in 1×10^4). C. D. KOPKIN

1263. **Reaction of nitrates and nitramines with phosphoric acid.** C. L. Whitman and M. I. Fauth (Research and Development Dept., U.S. Naval Powder Factory, Indian Head, Md., U.S.A.). *Anal. Chem.*, 1958, **30** (10), 1672–1673.—Inorganic nitrates react quantitatively with either H_3PO_4 or H_2SO_4, as shown by nitrometer experiments, whereas nitrate esters and nitramines react only partially or not at all with H_3PO_4. A qual. test based on reaction with diphenylamine in H_2SO_4 and in H_3PO_4 serves to differentiate nitramines from nitrates, nitrites, and nitrate esters. All these compounds show a positive reaction (purple coloration) when 0·01 g is dissolved in 1 ml of 50% H_2SO_4 and 0·2 ml of 0·2% diphenylamine in 70% H_2SO_4 is added. When the sample is dissolved in 1 ml of 60% H_3PO_4, and 0·2 ml of 0·2% diphenylamine in 85% H_3PO_4 is added, nitramines do not give a positive reaction. This serves to detect the presence of nitrates or nitrate esters in nitramines.
T. R. ANDREW

1264. **Quantitative determination of phosphoric acid. VIII. Chelatometric determination of phosphate by zinc ammonium phosphate - EDTA method.** Masayoshi Ishibashi and Masayuki Tabushi (Chem. Dept., Fac. of Sci., Kyoto Univ., Sakyo-ku). *Japan Analyst*, 1958, **7** (6), 376–380.—Since $ZnNH_4PO_4$ is sol. in an ammoniacal soln. of pH 10, its use for the chelatometric titration of phosphate is superior to the use of magnesium phosphate (*e.g.*, Flaschka *et al.*, *Z. anal. Chem.*, 1952, **135**, 333; 1953, **138**, 272; 1953, **141**, 364; *Mikrochim. Acta*, 1952, **39**, 38, 101). *Procedure*—The sample soln. containing 5 to 50 mg of P_2O_5 is mixed with NH_4Cl and *M* $ZnCl_2$ (an amount 2 to 5 times the equiv. of the P) to produce 2 to 3 *M* NH_4Cl soln., heated and made ammoniacal, with *p*-nitrophenol as indicator. The ppt. is filtered off after 3 hr., washed with cold water, dissolved in dil. HCl, neutralised with aq. NH_3 soln., made pH 10 with a buffer [70 g of NH_4Cl and 570 ml of aq. NH_3 (sp. gr. 0·88) per litre] (2 ml) and titrated with EDTA soln. (0·01 or 0·1 *M*), with Eriochrome black T as indicator. The presence of PO_4^{3-} does not vitiate the indication of the end-point. The error is $\pm 0{\cdot}3\%$. This method is applicable to the determination of P in ores. K. SAITO

1265. **Examination of experimental conditions for the colorimetric determination of phosphate by the molybdenum blue method.** Fumikazu Kawamura and Hiroshi Namiki (Fac. of Engng, Yokohama Univ., Minami-ku, Yokohama). *Japan Analyst*, 1958, **7** (4), 239–242.—The effect of concn. of H_2SO_4, ammonium molybdate (**I**) and $SnCl_2$ on the colorimetric determination of P was examined. The rate of development of colour decreases with H_2SO_4 concn., but the stability of the colour increases, the optimum concn. being 0·65 *N*. The concn. of $SnCl_2$ (< 1·2 ml of 2% soln.) affects the colorimetry only slightly, but the optimum concn. of **I** in the final soln. is 0·15%. K. SAITO

1266. **Studies on industrial analysis with X-ray diffractometer. V. Quantitative analysis of polyphosphates ($NaPO_3$ - $Na_5P_3O_{10}$ system) with a Geiger counter X-ray diffractometer.** Genzo Hashizume, Yuzi Hagino and Masamitu Kobayashi (Ind. Res. Inst., Hyogo Prefecture, Kamitezakicho, Suma-ku, Kobe). *Japan Analyst*, 1958, **7** (5), 287–292.—Amorphous polyphosphate in the system $NaPO_3$ - $Na_5P_3O_{10}$ is converted by heating into crystalline $NaPO_3$ and $Na_5P_3O_{10}$ (Partridge *et al.*, *J. Amer. Chem. Soc.*, 1941, **63**, 454; Liddell, *Ibid.*, 1949, **71**, 207), then covered with thin collodion film (to avoid contact with moist atmosphere) and submitted to diffraction measurement. The relative intensity of both the $NaPO_3$ peak $d = 3{\cdot}87$ Å and $Na_5P_3O_{10}$ peak $d = 4{\cdot}08$ to the internal standard $CaSO_4{\cdot}0{\cdot}5H_2O$ (peak $d = 6{\cdot}0$) is proportional to their wt. (%). The measurement of the peak area is preferred to that of the peak height, because the degree of crystallinity affects the former measurement only slightly. K. SAITO

1267. **Spectroscopic determination of arsenic in anthracite coal ashes.** R. H. Hall and H. L. Lovell (College of Mineral Industries, Pennsylvania State Univ., University Park, U.S.A.). *Anal. Chem.*, 1958, **30** (10), 1665–1669.—By the use of specially designed hollow electrodes having a small orifice (boiler electrodes) the sensitivity of the spectrographic technique for the determination of As has been enhanced. A 100-mg sample is mixed with 100 mg of carbon powder containing 0·4% of Sb_2O_3 and packed into the electrode. The intensity of the As line at 2349·84 Å is compared with that of the Sb line at 2612·30 Å, attenuated by means of a step sector. The third step of reduction of a seven-step sector with a step ratio of 1 to 1·585 is used. Spectra were recorded in the second order with 40 sec. exposure at 15 amp. Results on 14 samples containing 0·003 to 0·03% of As_2O_3 show a coefficient of variation of $\simeq 20\%$.
T. R. ANDREW

1268. **Gravimetric, volumetric and photometric methods for the determination of bismuth.** M. I. Ivanyutin and A. I. Busev. *Nauch. Dokl. Vŷssh. Shkolŷ, Khim. i Khim. Tekhnol.*, 1958, (1), 73–78; *Ref. Zhur., Khim.*, 1958, (19), Abstr. No. 64,221.—It is established that OO-diethyl phosphorodithioate (**I**) quant. precipitates Bi^{3+} from weakly acid soln. as a greenish-yellow ppt. of formula $[(C_2H_5O)_2PSS]_3Bi$ (**II**) of m.p. 55°; the solubility of **II** is $1{\cdot}4 \times 10^{-6}$ mole per litre, solubility product $1{\cdot}04 \times 10^{-32}$. In the presence of tartrates (pH 9 to 13) or EDTA (disodium salt) (pH 9), **I** does not precipitate Bi. Thiourea (**III**) in weakly acid soln. does not mask Bi^{3+}. The sensitivity of the reaction is 2 μg at a limiting dilution of 1 in 5×10^5. For the gravimetric determination of Bi^{3+}, precipitate from

a weakly acid (HNO_3 or H_2SO_4) soln. with a 1·2 to 1·5-fold excess of the nickel salt of **I**, collect the ppt. in a glass filter, wash it with water, dry and weigh. The Bi^{3+} may also be titrated, the end of the titration being determined potentiometrically with a platinum electrode coated with mercury. In this case 1·5 g of Ni, Mn, Cr, Al, Ba, Ca or Mg does not interfere in the determination of 0·1 g of Bi; Fe^{3+} interfere. In the photometric variation of the method, extract **II** with CCl_4 and measure the extinction of the extract at 330 or 400 mμ (in the former case, elements which are extracted as complexes with **I** interfere). At 400 mμ the extinction of the complexes of Pd and Cd with **I** is practically zero, and that of the complexes of Sb and Sn with **I** negligible. The interference caused by Cu may be removed by reduction to Cu^{I}. The methods described may be used for the determination of Bi, Cu and Pb in enriched dust. C. D. KOPKIN

1269. **Determination of vanadium in metals (ferrovanadium, vanadium alloys, etc.) and vanadic acids.** F. Nouyrigat (Lab. Centr. de Rech. des Établ. Kuhlmann, 95, rue Danton, Levallois-Perret, France). *Bull. Soc. Chim. France*, 1958, (6), 781–785.—Current methods of volumetric determination of V are investigated and criticised on the grounds of inaccuracy of the preliminary oxidation or reduction of the V to the V^{V} or V^{IV} oxidation state. It is shown that the methods are very dependent upon the operator. A potentiometric method is described which does not have this disadvantage. *Procedure*—A 50-ml aliquot of the soln. of the sample (in HNO_3 - H_2SO_4) is heated to 70° and 1% $KMnO_4$ soln. is added dropwise to a pink colour, followed by 5 ml of conc. H_2SO_4. Then $(NH_4)_2SO_4.FeSO_4$ soln. (just $< 0{\cdot}1\ N$) is added dropwise from a micro-burette until a point of inflection in the potential curve is obtained (destruction of excess of $KMnO_4$). Conc. H_3PO_4 (15 ml) is then added to sharpen the V^{IV} end-point and 50 ml of the standard $(NH_4)_2SO_4.FeSO_4$ soln. is added from a pipette. The titration is continued with the micro-burette to a new point of inflection (complete reduction of V^{V} to V^{IV}). The titre of the V is then the vol. of $(NH_4)_2SO_4.FeSO_4$ soln. added between the two points of inflection.
E. J. H. BIRCH

1270. **An accurate and rapid method for the simultaneous direct determination of the state of oxidation of vanadium and of the vanadium content of metal - vanadium - oxygen compounds.** B. Reuter and J. Siewert (Anorg.-chem. Inst., Technische Univ., Berlin). *Z. anal. Chem.*, 1958, **162** (3), 175–180.—To determine the state of oxidation of V, suspend the sample (200 mg) in 50% H_2SO_4 (10 ml) and slowly add a known vol. of 0·1 *N* $KMnO_4$ sufficient to dissolve the sample with the aid of heat; add conc. H_3PO_4 (5 ml), cool, dilute with H_2O to 100 ml and titrate with 0·1 *N* $FeSO_4$, with Na N-methyldiphenylamine-*p*-sulphonate as indicator. To the titrated soln. add a distinct excess of *N* $KMnO_4$, decolorise in the cold with 5% $NaNO_2$ soln. added with mechanical stirring, add urea (5 g), boil for 10 min., cool and determine the quantity of V by titration with 0·1 *N* $FeSO_4$ as described above. The error is $\simeq \pm 0{\cdot}1\%$.
A. R. ROGERS

1271. **The determination of nitrogen in vanadium metal.** U.K.A.E.A. Industrial Group, Chem. Services Dept. (Operations Branch, Springfields, Lancs.). U.K.A.E.A. Report IGO-AM/S-9, 1958, 6 pp.—The sample is attacked by H_2SO_4 (9 *M*) followed by H_2O_2 (100 vol.) to dissolve any residual nitride. The NH_3 is then steam-distilled from alkaline soln. and determined absorptiometrically with a Na phenoxide - NaOCl reagent for samples containing 5 to 90 p.p.m. of combined N and Nessler reagent for samples containing 90 p.p.m. to 2% of combined N. The method has a negative bias of 5% at the 5 to 90 p.p.m. level and a coeff. of variation of $\pm$ 5%. At the 300 to 600 p.p.m. level, the recoveries are quant. and the coeff. of variation is $\pm$3%. W. T. CARTER

1272. **Spectrochemical determination of tantalum in zirconium.** S. V. Elinson, K. I. Petrov and A. T. Rezova. *Zhur. Anal. Khim.*, 1958, **13** (5), 576–579.—Tantalum is determined spectrographically after extraction of the fluoride complex with *cyclo*hexanone from a soln. 2 to 4 *M* in H_2SO_4. With an equal vol. of *cyclo*hexanone, 3 extractions are sufficient. The organic solvent is removed by azeotropic distillation with water, to a final vol. of 2 to 3 ml. The Ta is determined from the line 2685·1 A. Molybdenum may be added as an internal standard, using the line 2688·0 A. Up to 10^{-3} % of Ta in 1 g of zirconium can be determined with a relative mean arithmetical error of 20%.
C. D. KOPKIN

1273. **Separation of small amounts of tantalum from titanium with pyrogallol.** A. P. Savostin and I. P. Alimarin. *Vestn. Moskov. Univ.*, 1958, (2), 211–215.—The experiments were carried out with the radioactive isotope ^{182}Ta. The mixtures of oxides (0·2 g, ratio of Ta to Ti = 1:122) were fused with $K_2S_2O_7$, the melt was extracted by heating with 50 ml of a 5% soln. of pyrogallol, 2 ml of aq. NH_3 (1:2) was added, and then water in an amount such that, after adding various amounts of acid, the soln. would have a total vol. of 100 ml. The soln. were heated and various amounts of HCl or HNO_3 added; most of the Ti was pptd., taking with it the Ta. The acid soln. were heated on a water bath for 10 to 15 min., set aside overnight, filtered through a dense paper and the ppt. ignited and fused with $K_2S_2O_7$. The melts were extracted with H_2SO_4 and Ti was determined colorimetrically as the complex with H_2O_2, and Ta determined radiometrically. At pH 1·9 to 4·5, between 83 and 101% of the Ta was pptd., the ratio of Ta to Ti in the ppt. varying from 1:12 to 1:76. Similar tests were carried out in the presence of NaF, with starting ratios of Ta to Ti of 1:122 and 1:1220, 5 ml of a soln. of NaF containing 100 mg of NaF being added to the leaching soln. The tests included single, double and triple pptn., the first separation being effected in a platinum vessel, with filtration through a waxed funnel. For multiple pptn., the ppt. after ignition were fused with $K_2S_2O_7$ and the melt leached with pyrogallol soln. as before. Best results were obtained when pptn. was carried out in soln. of acidity 0·5 to 1·0 *N* in HNO_3 or 0·5 to 2·0 *N* in HCl. On the average, triple pptn. gave 70 to 80% of the Ta in the final ppt. (ranging from 54% to 90%), the final ratio of Ta to Ti being 1:0·2 to 0·4 on the average (ranging from 1:0·19 to 1:0·70).
C. D. KOPKIN

1274. **Determination of sulphides, sulphites and thiosulphates when present together.** A. P. Kreshkov and L. P. Senetskaya. *Nauch. Dokl. Vyssh. Shkoly, Khim. i Khim. Tekhnol.*, 1958, (1), 68–72;

Ref. Zhur., Khim., 1958, (19), Abstr. No. 64,226.—The photometric determination of S^{2-} in the presence of SO_3^{2-} and $S_2O_3^{2-}$, without their preliminary removal, is based on the red colour formed by the reaction of S^{2-} with the mercury - diphenylcarbazone complex (**I**). To 1 or 2 ml of the soln. (containing 0·1 to 1 mg of S^{2-} per ml) add dropwise an aq. suspension of **I** [to 30 ml of a soln. of $Hg(NO_3)_2$ containing 10 mg of Hg per ml add 20 ml of a 1% ethanolic soln. of diphenylcarbazone, filter off the ppt., carefully wash it free of Hg, grind it in a mortar with 5 ml of water and add 1 ml of a 0·5% soln. of gelatin and 50 ml of water] until a negative nitroprusside reaction for S^{2-} is obtained. To the resulting soln. add 5 ml of a soln. of Na_2S (1 mg of S^{2-} per ml), make up to 100 ml with 1·2 or 1·5 *N* NaOH and measure the extinction with a green filter (immediately if the suspension of **I** is freshly prepared, or after 40 min. if it was prepared more than 24 hr. previously). The described method is satisfactorily accurate and rapid and may be used for the rapid determination of sulphides and sulphide S in minerals, ores, metals, alloys and other materials. C. D. KOPKIN

1275. **Determination of sulphur oxides in stack gases.** E. B. Seidman (Shell Oil Co., Wilmington, Calif., U.S.A.). *Anal. Chem.*, 1958, **30** (10), 1680–1682.—Sulphur trioxide is absorbed from a 1 cu. ft. sample by passage through an absorber containing 100 ml of 80% *iso*propyl alcohol, cooled in ice to prevent oxidation of SO_2; SO_2 is trapped in subsequent absorbers containing 25 ml of 3% H_2O_2 and 25 ml of 0·2 *N* NaOH. The *iso*propyl alcohol absorbent is diluted to 500 ml with *iso*propyl alcohol (80%) and a 25-ml aliquot is diluted with 25 ml of *iso*propyl alcohol (80%) and titrated with 0·01 *N* $BaCl_2$, 0·2% aq. thorin soln. being used as indicator. The alkaline peroxide soln. is boiled to destroy peroxide, acidified with HCl, boiled to remove CO_2 and diluted to 500 ml. After passage through a cation-exchange resin, a 10-ml portion is diluted with 40 ml of *iso*propyl alcohol and titrated as described above. T. R. ANDREW

1276. **The determination and the solubility of water in liquid sulphur dioxide.** D. Murakami and N. Tokura (Res. Inst. of Non-aq. Soln., Tohoku Univ., Katahira-cho, Sendai, Japan). *Bull. Chem. Soc. Japan*, 1958, **31** (4), 431–434 (in English).—The conductimetric estimation of water in liq. SO_2 is based on the Karl Fischer method. Several substances have been examined for their potential use as dehydrating agents for SO_2. The best of these was P_2O_5. C. A. SLATER

1277. **Indirect flame-spectrophotometric determination of sulphate sulphur.** W. M. Shaw (Univ. of Tennessee Agric. Exp. Sta., Knoxville, U.S.A.). *Anal. Chem.*, 1958, **30** (10), 1682–1689.—Barium may be determined flame-photometrically in the presence of 1000 mg of Na^+, K^+ or Mg^{2+} per litre by recording the photo-current at 515 mμ and deducting that due to the foreign-ion background at 522 mμ. Calcium, Sr^{2+} and Mn^{2+} show spectral interferences, resulting in negative errors (1000 mg of Ca per litre ≡ ≃ −7 mg of Ba per litre, 1000 mg of Sr ≡ ≃ −6 mg of Ba, and 1000 mg of Mn^{2+} ≡ ≃ −34 mg of Ba); Al^{3+}, Fe^{3+} and PO_4^{3-} should be separated by a modified basic acetate method. This procedure has been adapted to the determination of SO_4^{2-} in waters and soil extracts. Acidify the sample (containing 2 to 8 mg of S as SO_4^{2-}) with HCl and evaporate to dryness, destroying any organic matter in the residue by evaporating to dryness with H_2O_2 (5 ml of 15%). Add HCl (5 ml of 1·0 *N*) and boil, transfer the soln. to a 150-ml beaker, dilute to ≃100 ml and heat almost to boiling. Add dropwise $BaCl_2$ soln. (0·0625 *N*, 1 ml ≡ 1 mg of S) calculated to give an excess of 2 to 8 mg of Ba^{2+}, and digest until the vol. is reduced to 60 ml. Add acetate buffer (10 ml of 2 *N*, pH 4), $FeCl_3$ soln. (0·5 ml of *N* in 0·5 *N* HCl), HCl (4·5 ml of 1·0 *N*) and aq. NH_3 (10·0 ml of 1·0 *N*). Boil gently to reduce the vol. to 80 ml, cool, dilute to 100 ml and filter; use the filtrate for flame-photometric measurements. Results on 15 samples of water are in good agreement with gravimetric figures. T. R. ANDREW

1278. **Dissolution of sulphuric acid from an acid-form cation-exchange resin. The effect on the determination of sulphate ions.** Kunihiko Watanuki (Chem. Dept., Fac. of Engng, Tokyo Univ., Hongo). *Japan Analyst*, 1958, **7** (6), 385–386.—A significant amount of SO_4^{2-} dissolves from the acid-form cation-exchange resin Dowex 50-X12 (100 to 200 mesh) conditioned with 2 *M* NaCl, 2 *M* NH_4NO_3 and 4 *N* HCl. For the removal of interfering cations from natural water, the use of the Na or K form is recommended. When the acid form is used, the column must be conditioned immediately before use. K. SAITO

1279. **Contribution to the analysis and chemistry of the dithionites.** E. Schulek and L. Maros (L. Eötvös Univ., Budapest, Hungary). *Acta Chim. Acad. Sci. Hung.*, 1958, **17** (3), 273–287 (in German).—A method for the determination of $S_2O_4^{2-}$, $S_2O_3^{2-}$, $S_2O_5^{2-}$, and SO_3 in the presence of each other is based on the disproportionation of $S_2O_4^{2-}$ into $S_2O_5^{2-}$ and $S_2O_3^{2-}$ when heated in neutral aq. soln., the $S_2O_5^{2-}$ and $S_2O_3^{2-}$ originally present remaining unchanged. The iodine consumption by dithionite is different before and after disproportionation, which also enables the total quantity of the other compounds to be determined. After disproportionation, the $S_2O_5^{2-}$ and SO_2 content can be measured by titration with NaOH soln., with thymolphthalein as indicator. After titration, the combined quantity of $S_2O_4^{2-}$ and $S_2O_3^{2-}$ is determined by addition of $AgNO_3$ and H_2O_2, followed by titration of the H_2SO_4 formed. From the data obtained, the concn. of the individual components can be calculated. The accuracy is approx. ± 0·5%. G. P. COOK

1280. **Complexometric titration of selenium.** Shao-Lin Liu and Ming-Ing Chang (Dept. of Chem., Nanking Univ.). *Acta Chim. Sinica*, 1958, **24** (4), 306–310.—Selenate may be quant. pptd. as $PbSeO_4$ with $Pb(NO_3)_2$ at a pH of 2 to 3 in 30% ethanol. The pptd. Pb is dissolved in an alkaline buffer soln. containing ascorbic acid and excess of standard EDTA soln. which is subsequently back-titrated with standard manganous soln., with Eriochrome black T as indicator. If Se is present in the form of selenite, it should be previously oxidised to selenate by boiling with $KMnO_4$ soln., the excess of which is destroyed with H_2O_2. The proposed method for the determination of Se is rapid and accurate. Small amounts of Cu^{2+}, Fe^{3+}, Ni^{2+}, Co^{2+} and TeO_4^{2-} do not interfere, but Bi^{3+}, Hg^{2+}, SO_4^{2-} and AsO_4^{3-} must be absent. S. H. YUEN

1281. **The polarographic determination of selenium in signal glass.** A. Cioară and L. Cariadi.

Acad. R.P.R., Stud. Cercet. Chim., 1958, **6** (1), 7–24.—The quantities of the components necessary for the red colour in signal glass after melting are 0·03% of Se; 0·06% of Cd; 0·03% of S. The determination takes account of the interference by Cd in the polarographic determination of Se, and the fact that previous pptn. of Cd in acid soln. results also in loss of Se. Therefore the Se is separated from Cd, etc., by reduction of selenous acid with Na_2SO_3 in the presence of HCl. The metallic Se is filtered off, and re-oxidised with HNO_3 to the acid; after which it is buffered with a soln. of NH_4Cl (0·2 *N*) and aq. NH_3 to a pH of 8·5. Other ions from the soln. of the glass, *e.g.*, Fe^{3+}, Al^{3+}, Ca^{2+}, Mg^{2+} and SO_4^{2-}, do not interfere, but NO_3^- does. *Procedure*—The finely ground glass (1 g) is treated in a platinum crucible with H_2O (2 ml), HNO_3 (1:1) (2 ml), H_2SO_4 (1:1) (1 ml) and HF (40%) (25 ml). The mixture is evaporated on a water bath at $>70°$, cooled and treated with HF (40%) (10 ml), and re-evaporated, and the residue is dissolved in 20 ml of boiling H_2O and filtered. The filtrate is again evaporated on a water bath at $>70°$; the residue is cooled and treated with 3 g of Na_2SO_3 and HCl (conc.) is added until the residue is covered. The red ppt. of Se is filtered off after 1 hr. The combined soln. and washings are evaporated to dryness on a water bath at $>70°$, and this is repeated twice. The final white residue of selenous acid is dissolved in warm H_2O and diluted to 25 ml, and 1 to 3 ml is pipetted into a polarographic cell together with 1 ml of *N* NH_4Cl, 0·1 ml of 0·9 *N* aq. NH_3, 0·1 ml of a freshly prepared satd. soln. of Na_2SO_3 and H_2O to 5 ml. The polarographic curve is then drawn for the region -1 to 1·8 V. The amount of Se present is then calculated either from the corresponding figure read off a standard diagram, or by adding to the polarographic cell a sufficient vol. of standard soln. to increase the $E_{\frac{1}{4}}$ by 10 to 20 mm under the same conditions. The formulae for both calculations are given. H. SHER

1282. **Turbidimetric determination of a micro amount of sulphur in selenium.** Shigeru Yokosuka and Shoichi Shirakawa (Bessi Mine Office, Sumitomo Mining Co., Niihama, Ehime-ken). *Japan Analyst*, 1958, **7** (6), 363–368.—The extinction (372 mμ) of a suspension of $BaSO_4$ in an aq. system containing 65% (v/v) of a mixture of ethanol and propane-1:2-diol (1 + 1, by vol.) and 0·15 *M* HNO_3 and 0·125 *M* $BaCl_2$ is proportional to the concn. of S (<100 μg) and remains unchanged for 40 min. Iron and Sb interfere but are pptd. (together with As, Bi, Sn, Si, Te and Al) with aq. NH_3 soln. The results compare favourably with those of Bechhold's method (*J. Res. Nat. Bur. Stand.*, 1936, **16**, 555; *Kolloid Z.*, 1922, **31**, 70), which makes use of a mixture of glycerol and ethanol. *Procedure*—Dissolve the sample (<100 mesh, 2 g) in aqua regia (20 ml) and evaporate to dryness, first with $NaNO_3$ (10 mg of Na per ml) (5 ml) and then with HBr (sp. gr. 1·48, 20 ml) to volatilise any Se. Repeat the treatment with HBr twice (5 ml each) and again evaporate to dryness with HNO_3 (5 ml). Add 0·3 *M* HNO_3 (10 ml) containing 65% (v/v) of the mixture of ethanol and propane-1:2-diol and mix a 5-ml portion with 0·25 *M* $BaCl_2$ (5 ml) containing 65% of the alcohol mixture at <20°. Measure the extinction at 372 mμ after 15 min. In the presence of Fe, etc., dilute the HNO_3 soln. (5 ml) (after the removal of Se) with aq. NH_3 soln. and water (20 ml) and filter. Evaporate the filtrate to dryness with HNO_3, and mix with the solvent as mentioned above. K. SAITO

1283. **Determination of impurities in industrial selenium.** V. Barcanescu, E. Potamian and V. Bartos. *Rev. Chim., Bucharest*, 1958, **9** (6), 307–310.—A detailed graphical scheme of separation of Se, based on the dissolution of the sample in HNO_3 and subsequent treatment with aq. NH_3 and solid Na_2S, is given. Details are also given of the determination of Te, S and As in selenium. H. SHER

1284. **Separation of quadrivalent and sexavalent tellurium with tributyl phosphate in kerosine.** Mariko Inarida (Chem. Dept., Fac. of Sci., Tokyo Univ., Hongo). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1958, **79** (6), 696–698.—Whereas Te^{IV} is quant. extracted with tributyl phosphate in kerosine (20%) from 4 to 10 *N* HCl, Te^{VI} remains in the aq. phase. The use of two portions (5 ml each) of the reagent suffices for the separation of <10 mg of Te^{IV} from <10 mg of Te^{VI}. This method is applicable to the separation of tracer-scale amounts of Te in these valency states. K. SAITO

1285. **Chronometric determination of sexavalent molybdenum with tungsten and other electrodes.** A. I. Busev and Li Gyn (M. V. Lomonosov Moscow State Univ.). *Zhur. Anal. Khim.*, 1958, **13** (5), 519–527.—The chronometric titration of Mo^{VI} in HCl and H_2SO_4 soln. with a soln. of Cr^{2+}, with platinum, mercury, amalgamated platinum, tungsten, graphite and tantalum electrodes is studied. In general, two sharp changes of potential are observed, corresponding to the reductions $Mo^{VI} \rightarrow Mo^{V}$ and $Mo^{V} \rightarrow Mo^{III}$. Titration curves are given. The tungsten indicator electrode is the most suitable, and titration curves show the effect of different concn. of acid. In H_2SO_4, Mo may be titrated using the tungsten electrode by means of the first change of potential and in HCl by both the first and second changes. In the presence of Fe and Cu, two changes of potential are observed, the first after the simultaneous reductions to Mo^{V}, Fe^{II} and Cu^{I} and the second after the reduction of Mo^{V} to Mo^{III}, after which Cu^{I} is reduced to metallic copper. The Mo may be determined by the quantity of titrant used between the first and second changes of potential; Fe and Cu cannot be determined. To determine Fe and Mo in the presence and absence of Cu, begin the titration in 4% H_2SO_4 in an atmosphere of CO_2 at room temp. The Fe^{III} is first reduced, giving a small but clear change of potential; then the reductions $Mo^{VI} \rightarrow Mo^{V}$ and $Cu^{II} \rightarrow Cu^{I}$ take place, at the end of which there is observed a large change of potential, the position of which, however, is poorly reproducible. After this change of potential add to the soln. 100 ml of conc. HCl saturated with CO_2, warm to between 60° and 70° and continue the titration to a third change of potential, corresponding to the reduction to Mo^{III}; the quantity of $CrCl_2$ soln. used between the second and third jumps gives the amount of Mo present. Satisfactory results are obtained for Mo and Fe, but not for Cu. C. D. KOPKIN

1286. **The determination of combined nitrogen in molybdenum metal. (Modified Allen method.)** U.K.A.E.A. Industrial Group, Chem. Services Dept. (Operations Branch, Springfields, Lancs.). U.K.A.E.A. Report IGO-AM/S-43, 1958, 4 pp.—The sample is dissolved in hot H_2SO_4 (18 *M*) and oxidised to molybdic oxide with H_2O_2 (100 vol.).

The NH_3 is steam-distilled from alkaline solution and determined absorptiometrically with Na phenoxide - NaOCl reagent. The method is intended for samples containing between 20 p.p.m. and 0·5% of combined nitrogen and has a negative bias of 10% at the 50 p.p.m. level. At the 400 p.p.m. level the results are quant., with a coeff. of variation of ±4%. W. T. CARTER

1287. **Colorimetric determination of tungsten in scheelite ores and mill products.** R. P. Hope (Kang Island Scheelite Ltd.). *Proc. Aust. Inst. Min. Metall.*, 1958, (185), 51–64.—The finely ground sample (0·2 to 2·0 g) is fused in an iron crucible with ≃15 g of NaOH at a dull red heat (the fusion must not be allowed to become too hot), the melt is decomposed with ≃80 ml of nearly boiling water, the soln. is filtered and made up to the required vol. An aliquot containing 0·05 to 0·6 mg of WO_3 is introduced into a 50-ml flask, 5 ml of conc. H_2SO_4 is added, followed, after cooling, by 10 ml of conc. HCl, and 25 ml of 4 *M* $SnCl_2$ in conc. HCl. The flask is cooled to ≃20°, filled to the mark with 5% aq. NH_4SCN and the soln. is transferred to a small beaker. After 30 min. the colour is measured absorptiometrically with filters having max. absorption at 400 mμ. The reduced tungsten soln. must not be allowed to stand longer than 20 to 30 min. for colour development, since otherwise back-oxidation may occur. Fifteen determinations performed on a soln. of a gravity tailing gave a mean value of 0·111% of WO_3 with a standard deviation of ±0·002. The method is based on that of Freund *et al.* (*Anal. Chem.*, 1951, **23**, 781) the principal modifications being an increase in the strength of the $SnCl_2$ soln. from 2 *M* to 4 *M* to counteract the interference of iron and the use of NH_4SCN instead of KSCN because it appears to be more stable in soln.

J. M. JACOBS

1288. **Chemical analysis of calcium tungstate.** Š. Král and J. Vobora (SONP, Kladno, Czechoslovakia). *Hutn. Listy*, 1958, **13** (5), 429–430.—The sample is decomposed by fusion with Na_2CO_3; W, Mo, Al, Cr, V and P are determined in the filtrate and Ca, Mg, Ti, Mn and Fe in the residue. Arsenic, Sn, Cu, C, S and Si, which may be present in 0·001% concn., can be determined in another portion of the sample. Tungsten is determined gravimetrically with cinchonine or mercurous nitrate, Al gravimetrically as Al_2O_3 or, in samples containing >0·1% of P_2O_5, as $AlPO_4$. For Mo a photometric method with KSCN and $SnCl_2$ in K Na tartrate medium (masking of W) is suggested; Cr is determined by oxidimetric titration, V by titration with $FeSO_4$, and P gravimetrically as $AlPO_4$ or molybdophosphate. The residue from the fusion is dissolved in HCl, and Fe is determined colorimetrically with KSCN, Ti with H_2O_2, Mn by the Procter-Smith method, Ca by an indirect complexometric titration in a soln. of triethanolamine, with the use of thymolphthalexone as indicator, Mg complexometrically at pH 10 with Eriochrome black T as indicator, Si gravimetrically, As titrimetrically with $KBrO_3$ soln. (after distillation), Cu photometrically with aq. NH_3 or by potentiometric titration with KCN soln., Sn polarographically in an acid soln. of NH_4Cl and hydrazine sulphate, C as CO_2, and S gravimetrically as $BaSO_4$. Detailed procedures are given. J. ZÝKA

1289. **Reaction of tungstates with some organic hydroxy compounds, mainly with sugars.** E. Plško (Dept. Inorg. Chem., Chem. Inst., Acad. Sci., Bratislava, Czechoslovakia). *Chem. Zvesti*, 1958, **12** (5), 312–315.—Tungstate added to a soln. of sucrose, maltose, lactose, glucose, glycerol, Na tartrate, fructose, dulcitol or sorbitol causes a rise in the pH value as the result of the formation of a complex compound. The use of phenolphthalein in the soln. enables the sensitivity of the reaction to be studied. When sorbitol is used as reagent the method is suitable for detecting 3×10^{-4} *M* soln. of tungstates. Molybdates react similarly, but the sensitivity is lower. The mechanism of the reaction is discussed. J. ZÝKA

1290. **Determination of uranium with potassium iodate.** E. S. Przheval'skii, E. R. Nikolaeva and N. I. Udal'tsova (V.I. Vernadskii Inst. of Geochem. and Anal. Chem., Acad. Sci., USSR, Moscow). *Zhur. Anal. Khim.*, 1958, **13** (5), 567–569.—Uranium may be determined as the tetra-iodate by obtaining U^{IV} electrolytically on the mercury cathode (Alimarin *et al.*, *Zhur. Anal. Khim.*, 1958, **13**, 464), adding to 15 to 30 ml of the soln. one-half of its vol. of a 10% soln. of KIO_3 in 10% H_2SO_4 (for 5 mg of U and above) or two-thirds of its vol. of this soln. (for smaller amounts of U, *e.g.*, 1 to 2 mg), followed by twice the vol. of the original soln. of a 0·8% soln. of KIO_3 in 2% H_2SO_4. Filter off the ppt. on a glass filter and wash it successively with a 0·4% soln. of KIO_3 in 1% H_2SO_4, ethanol and ether, and dry to const. wt. at 100° to 120°. The ppt. has the composition $U(IO_3)_4$ and has no water of crystallisation when dried at 110° to 120°. For the volumetric method, dissolve the washed ppt. in 20 ml of 10% H_2SO_4, add 20 ml of a 5% soln. of KI and titrate the liberated iodine with thiosulphate. Part of the iodine reacts with the uranium—

$$U^{4+} + I_2 + 2H_2O \rightarrow UO_2^{2+} + 2I^- + 4H^+,$$

so that 1 atom of U is equiv. to 22 gram-equiv. of iodine. The errors obtained by the gravimetric and volumetric methods were on the average ±1·0% and ±0·6%, respectively. The presence of up to a 50-fold excess of Al does not cause interference; Fe^{3+} even in small amounts cause incomplete pptn. of U. Under the pptn. conditions Cu and Mo do not form iodates and may be removed by electrolysis on the mercury cathode. Vanadium is reduced by the electrolysis but is not precipitated with the $U(IO_3)_4$. C. D. KOPKIN

1291. **Determination of uranium by a spot developed on filter-paper.** Shunji Umemoto, Michio Ichikawa and Shosuke Watanabe (Balneological Lab., Okayama Univ., Misasa, Tottori-ken). *Japan Analyst*, 1958, **7** (4), 228–231.—Uranium in ores is extracted with ethyl acetate from HNO_3 soln. in the presence of $Al(NO_3)_3$ (Guest and Zimmerman, *Anal. Abstr.*, 1955, **2**, 3048) and spotted on a filter-paper (0·05 ml) to produce an ellipsoid (long diameter ≃30 mm). The paper is dried, immersed in 2 % $K_4Fe(CN)_6$ soln. for 20 sec., washed with running water for 10 sec., dried in the absence of light, and treated with molten paraffin wax on a water bath. The extinction of the spot is measured against blank filter-paper, treated with the paraffin wax, at 460 mμ (max. absorption, 395 mμ). The working curve is not linear but is reproducible for a given paper under given conditions. The error is <10% for uranium ores of sedimentary origin. K. SAITO

1292. **Simple determination of uranium by frontal paper chromatography.** Masanobu Sakanoue (Balneological Lab., Okayama Univ., Misasa, Tottori-ken).

Japan Analyst, 1958, **7** (5), 292–296.—In order to increase the sensitivity of the quant. paper-chromatographic determination of U with $K_4Fe(CN)_6$ (Hunt *et al.*, *Analyst*, 1955, **80**, 172), some improvements are suggested. Ores are treated with dil. HNO_3 (1 + 3) containing $Al(NO_3)_3$ (500 g of nonahydrate per 400 ml of the HNO_3) (2 ml) in a boiling-water bath for 1 hr. One drop of this extract (containing >0·02 μg of U) is spotted on a filter-paper (1 cm × 40 cm) at a point 5 cm from the lower end. The paper is dried at 60° for 8 min. and a few drops of 30% $K_4Fe(CN)_6$ soln. are placed on a zone 14 cm from the lower end. The uranyl spot is developed with ethyl acetate for 3 hr., washed with running water for 10 sec., dried and immersed in molten paraffin wax to fix the colour spot, which is compared with those prepared from standard soln. No interference results from Fe, Cu, Ni, Th and Al. The error is <30%.

K. SAITO

1293. **Resorcinol as a reagent for the spectrophotometric determination of uranium.** P. C. Jain and G. S. Rao (Univ. of Saugar, India). *Curr. Sci.*, 1958, **27** (9), 340.—Aq. soln. of uranyl acetate (0·025 *M*) and resorcinol (0·05 *M*) interact to produce a red to deep-red soln. which shows appreciable absorption at 400 to 410 mμ according to the concn. of UO_2^{2+}. There is little change in extinction of the soln. even after 48 hr. or after heating to about 60°. Attempts to determine the composition of the coloured product failed. The system obeys Beer's law at a concn. of UO_2^{2+} of between $0·125 \times 10^{-3}$ *M* and $1·25 \times 10^{-3}$ *M*.

K. R. C.

1294. **Radiometric determination of uranium-234.** H. Bussell, D. Huber and L. C. Nelson. *U.S. Atomic Energy Comm.*, Rep. NBL-143, 1958, 44–50.—This radiochemical method involves the quant. electro-deposition of U_3O_8 (about 500 μg) on to a platinum disc (1 to 1·5 in. in diam.). After ≃1 hr., the U on the disc is counted in an α-proportional-counter and the amount of ^{234}U is calculated. The completeness of the electro-deposition is determined by making a fluorimetric measurement of the soln. after deposition. With a 93% standard, the average calculated ^{234}U content is 1·025% and the standard deviation is ±0·014%. With an 88% standard, the average calculated ^{234}U content is 0·992% and the standard deviation is ±0·01%.

K. R. C.

1295. **Separation of uranium and vanadium.** Yu. V. Morachevskiĭ, A. I. Belyaeva and L. V. Ivanova (A. A. Zhdanov Leningrad State Univ.). *Zhur. Anal. Khim.*, 1958, **13** (5), 570–575.—Experiment has shown that the separation of U and V is most completely effected in strongly acid or strongly alkaline media. Thus under suitable conditions cupferron may be used. The phosphate method is less satisfactory, but the use of excess of ammonium phosphate and alkaline soln. allows the separation to be effected. In separating U from large amounts of alkaline and alkaline-earth metals, use may be made of the low solubility of their uranyl metavanadates. Uranium may similarly be separated from very dilute soln. These processes are effected by adding to the soln. a 1 to 3-fold excess of ammonium metavanadate, slightly acidifying (to pH 3·5 to 7) and heating to boiling.

C. D. KOPKIN

1296. **The spectrographic determination of calcium in uranium metal.** U.K.A.E.A. Industrial Group, Chem. Services Dept. (Operations Branch, Springfields, Lancs.). U.K.A.E.A. Report IGO-AM/S-118, 1958, 7 pp.—The metal is ignited to U_3O_8 and arced on copper electrodes at 7 amp. The spectra are recorded in a Jarrell-Ash fully automatic grating spectrograph, with Ilford Thin Film Half Tone plates. The method is suitable for calcium concn. in the range 5 to 200 p.p.m.

W. T. CARTER

1297. **Absorptiometric determination of boron in uranium metal.** U.K.A.E.A. Industrial Branch, Chem. Services. Dept. (Operations Branch, Springfields, Lancs.). U.K.A.E.A. Report IGO-AM/S-124, 1958, 15 pp.—Details are given of procedures and apparatus for dissolving the uranium in HCl and HNO_3 and the separation by distillation of the B as methyl borate after the addition of $AlCl_3$ soln. The B in the distillate is determined absorptiometrically as its curcumin complex which is produced under closely controlled conditions. The method is suitable for uranium with a content of B of 0·01 to 0·3 p.p.m.

G. J. HUNTER

1298. **Spectrographic determination of aluminium in uranium metal.** U.K.A.E.A. Industrial Group, Chem. Services Dept. (Operations Branch, Springfields, Lancs.). U.K.A.E.A. Report IGO-AM/S-125, 1958, 10 pp.—The uranium is converted by ignition into U_3O_8 and 100 mg of a mixture of the latter with 5% w/w of NaF is placed in a graphite cup (illustrated), above which is mounted a pointed graphite electrode. A large quartz spectrograph is set to the range 2500 to 3700 A and an arc current of 12 amp. is passed for 45 sec. The spectra from standard mixtures appropriate to the content of Al are recorded on the same photographic plate. For contents of Al of 5 to 200 p.p.m. the precision for duplicate determinations is ±25% (95% confidence limits); the corresponding value for quadruplicate determinations of contents from 200 to 1500 p.p.m. is ±15%.

G. J. HUNTER

1299. **The absorptiometric determination of combined nitrogen in uranium metal including swarf and powder.** U.K.A.E.A. Industrial Group, Chem. Services Dept. (Operations Branch, Springfields, Lancs.). U.K.A.E.A. Report IGO-AM/S-121, 1958, 8 pp.—After surface cleaning, the sample is dissolved in HCl (1:1), followed by $HClO_4$. An aliquot of the soln. is steam-distilled after making alkaline and NH_3 is determined absorptiometrically in the distillate with Na phenoxide - NaOCl reagent. The method is suitable for the determination of N in the range 5 to 150 p.p.m. and the precision in the range of 20 to 70 p.p.m. is ±13%.

W. T. CARTER

1300. **The absorptiometric determination of phosphorus in uranium metal.** U.K.A.E.A. Industrial Group, Chem. Services Dept. (Operations Branch, Springfields, Lancs.). U.K.A.E.A. Report IGO-AM/S-122, 1958, 5 pp.—The sample (1 g) is dissolved in conc. HNO_3 (5 ml); after evaporation of the soln. to dryness the residue is dissolved in water (10 ml). Aq. NH_3 soln. (1 + 3) is added to produce a permanent opalescence; ammonium molybdate reagent (**I**) (5 ml) is then added followed by 15% Na_2SO_3 soln. (1 ml) and 1% $SnCl_2$ soln. (0·5 ml). After dilution to 50 ml the soln. is allowed to stand for 5 min. and then the absorbancy is measured; Ilford 608 filters and a 4-cm cell are used. **I** is prepared by adding 300 ml of 20% H_2SO_4 to 5 g of ammonium molybdate dissolved in 200 ml of

water. The method is suitable for samples containing from 1 to 10 μg of P; the coeff. of variation is $<2\%$ for the upper part of the range. Up to 500 μg of Si does not interfere, but As must be absent. G. J. HUNTER

1301. **Absorptiometric determination of molybdenum in uranium metal.** U.K.A.E.A. Industrial Group, Chem. Services Dept. (Operations Branch, Springfields, Lancs.). U.K.A.E.A. Report IGO-AM/S-120, 1958, 5 pp.—To the sample (1 g) is added HCl (1 + 1) (10 ml) and then H_2O_2 to complete dissolution. After evaporation to dryness and resolution in water, aq. NH_3 is added to produce a ppt. which is redissolved by adding HCl; more HCl (2 ml) is then added and the soln. is diluted to 40 ml. After the addition of 5% KSCN soln. (10 ml), 5% $NaNO_2$ soln. (2 ml) and 10% $SnCl_2$ soln. (8 ml) the mixture is allowed to stand for 1 to 2 min. and is then extracted with extraction solvent (**I**) (40 ml) and the extinction of the organic phase is measured in a Spekker absorptiometer with Ilford 602 filters. The content of Mo is derived from a calibration graph. **I** is a mixture of ether and light petroleum (boiling-range 100° to 125°) (2:1); before use 100 ml of it is extracted with a mixture of 5% KSCN soln. (10 ml) and 10% $SnCl_2$ (10 ml). The coeff. of variation for contents of Mo of 20 to 30 p.p.m. is about $\pm 15\%$. G. J. HUNTER

1302. **Colorimetric determination of traces of bromine in uranium compounds.** M. W. Lerner. *U.S. Atomic Energy Comm.*, Rep. NBL-143, 1958, 9 pp.—Traces of Br are determined in $UO_2(NO_3)_2$ and hydrolysed UF_6 soln. *Procedure*—A simultaneous oxidation of bromide with HNO_3 and $KMnO_4$ is followed by extraction of the bromine with CCl_4; the Br is allowed to react with fluorescein to form eosin, which is then determined spectrophotometrically. For substances which dissolve less readily, such as UO_2, UO_3 and UF_4, a preliminary distillation is essential. Recoveries of either bromide or bromate added in 10-μg quantities to 2 to 5-g samples of hydrolysed UF_6 and $UO_2(NO_3)_2.6H_2O$ ranged from 95 to 100%. Recoveries of 4-μg quantities added to 2-g samples of UF_6 are tabulated. With the distillation procedure, recoveries of either bromide or bromate added in 10-μg quantities to 5-g samples of UO_2, UO_3, UF_4 and U_3O_8 ranged from 95 to 100%. K. R. C.

1303. **The absorptiometric determination of manganese in uranium metal.** U.K.A.E.A. Industrial Group, Chem. Services Dept. (Operations Branch, Springfields, Lancs.). U.K.A.E.A. Report IGO-AM/S-119, 1958, 5 pp.—The sample is dissolved in HNO_3 (1:1) and sufficient ammonium citrate is added to complex all the uranium. The Mn is extracted with $CHCl_3$ as the Na diethyldithiocarbamate complex at pH 8·2 to 8·6. The $CHCl_3$ is evaporated to dryness, organic matter is destroyed by heating with HNO_3 and H_2SO_4 and the Mn is converted into permanganate by boiling with KIO_4 in the presence of platinum gauze. The determination is completed absorptiometrically. The method is intended for concn. of Mn in the range 1 to 40 p.p.m. The precision at the 25 p.p.m. level is $\pm 10\%$ and in the range 1 to 25 p.p.m. the results tend to be 10 to 15% low. W. T. CARTER

1304. **A rapid method for the absorptiometric determination of iron in uranium metal.** U.K.A.E.A. Industrial Group, Chem. Services Dept. (Operations Branch, Springfields, Lancs.). U.K.A.E.A. Report IGO-AM/S-49, 1958, 8 pp.—The sample of turnings (1 g) is treated with HCl (3 + 7); after the initial reaction 7-vol. H_2O_2 (10 ml) is added and the soln. is boiled. After the addition of 10% Na_2SO_3 soln. (10 ml) the soln. is boiled again. Thioglycollic acid reagent (**I**) (5 ml) is then added, followed by aq. NH_3 until the soln. is orange and an ammonium carbonate soln. (2·5 g of solid dissolved in 25 ml of 6% aq. NH_3). After dilution to 100 ml the soln. is shaken and the absorbancy is then measured within 1 min.; Ilford 605 filters and a 4-cm cell are used. The content of Fe is derived from a standard curve; this is prepared by adding to known amounts of Fe, 20% thioglycollic acid (1 ml), aq. NH_3 until the soln. is pink and 1·5 ml in excess; after dilution to 100 ml the absorbancies of the soln. are measured. **I** is prepared by dissolving citric acid (180 g) in water (500 ml) and adding aq. NH_3 until the soln. is just alkaline; after cooling, 75% thioglycollic acid (55 ml) is added and the soln. is diluted to 1 litre. The standard deviation is ± 6 p.p.m. at the 250 and 500 p.p.m. levels. A detailed description of a cleaning procedure for uranium turnings is given. G. J. HUNTER

1305. **The absorptiometric determination of nickel in uranium metal.** U.K.A.E.A. Industrial Group, Chem. Services Dept. (Operations Branch, Springfields, Lancs.). U.K.A.E.A. Report IGO-AM/S-42, 1958, 6 pp.—The sample (50 g) is dissolved in HNO_3 (1:1) and residual insoluble matter is brought into solution by fusion with potassium bisulphate. An aliquot is taken and the nickel is extracted with $CHCl_3$ as the dimethylglyoxime complex from alkaline soln., re-extracted into aq. soln. with HCl (0·5 *M*) and determined absorptiometrically as the oxidised dimethylglyoxime complex. The method is suitable for analysing uranium containing 5 to 70 p.p.m. of nickel, and in the range 40 to 70 p.p.m. the precision is $\pm 27\%$. W. T. CARTER

1306. **Isotopic analysis of americium and curium by mass spectrometer.** D. F. Dance (A.E.R.E., Harwell, England). A.E.R.E. Report C/M 366, 1958, 3 pp.—Americium ($\simeq 10^{-8}$ g) and Cm ($\simeq 10^{-9}$ g) have been examined by using a Metropolitan-Vickers Type MS5 spectrometer. A coeff. of variation, based on 10 readings, of $\simeq 10\%$ was attained for abundances of $\simeq 2\%$. G. J. HUNTER

1307. **Quantitative determination of fluorine by formation of hydroxytrifluoroborates.** A. L. Gol'dinov, V. I. Lukhovitskiĭ, M. A. Gorovits and B. S. Roginskaya. *Zhur. Anal. Khim.*, 1958, **13** (5), 583–585.—Fluorine is determined by the conductimetric titration with HCl of the sodium tetraborate formed by the reaction—

$$3NaF + 5H_2BO_3 = NaBF_3OH + Na_2B_4O_7 + 7H_2O.$$

The results obtained are low by 2 to 5%; this may be prevented by adding to the soln. an equal vol. of ethanol. The error is then $\pm 0{\cdot}3\%$ for amounts of F down to 0·1 g, or $\pm 0{\cdot}8\%$ for 0·02 to 0·04 g of F. The presence of anions of strong acids (SO_4^{2-}, NO_3^-, Cl^-) in amounts up to 1 mole per mole of F increases the relative error to 1%; larger amounts give an error of up to 4%. The anions of weak acids interfere. The method may be used for the determination of F in the fluorides of Co, Mn and Sb. C. D. KOPKIN

1308. **The determination of fluoride in plutonium fluorides.** B. B. Murray (E.I. du Pont de Nemours & Co., Inc., Wilmington, Del., U.S.A.). *U.S.*

Atomic Energy Comm., Rep. DP-247, 1957, 11 pp.—Fluorosilicic acid was steam-distilled from samples in 12 *M* H_2SO_4 at boiling-point and the distillate was then titrated to a visual end-point with a standard soln. of $Th(NO_3)_4$. In the analysis of PuF_3, the average recovery of fluoride was 98·6% of the theoretical and the coeff. of variation of results was ±1·3%. K. R. C.

1309. **Volumetric determination of chlorine in silicate rocks.** Shigeki Kobayashi (Sugiyama Women's College, Yamazoe-cho, Chikusa-ku, Nagoya). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1958, **79** (5), 546–550.—Chlorine (<1 mg) in silicate rocks is pptd. as AgCl by the usual method, the ppt. is dissolved in KCN soln. (0·1%, 2 ml), treated with $KMnO_4$ in H_2SO_4 and the Ag^+ titrated by the Volhard method. The decomposition of $Ag(CN)_2^-$ with 0·1 *N* $KMnO_4$ (1 ml for 200 μg of Ag; 3 ml for <850 μg) in 2 *N* H_2SO_4 is readily effected on a water bath. The CN^- and Cl^- are expelled by heating the product to dryness. The excess of $KMnO_4$ is reduced with a few drops of 60% formic acid. The presence of Mn^{2+} and H_2SO_4 does not affect the titration with KSCN. K. Saito

1310. **The determination of the chlorine ion in turbid and strongly coloured solutions.** T. N. Dumitru. *Rev. Chim., Bucharest*, 1958, **9** (6), 325–326.—When chlorine is titrated with $Hg(NO_3)_2$ in the presence of HNO_3, an excess of Hg^{2+} is detected with the internal indicator diphenylcarbazone (**I**). *Procedure*—To the soln. (about 40 ml) are added 10 drops of indicator (satd. soln. of **I** in 95% ethanol) together with 4 ml of 0·2 *N* HNO_3 and 2 to 3 ml of benzene, and the mixture is shaken vigorously. Titration with $Hg(NO_3)_2$ soln. (0·01 *N* acidified with HNO_3) is carried out with continuous agitation. The benzene layer changes from violet - rose to intense violet - blue at the end-point. H. Sher

1311. **Separation of iodine and tellurium by extraction with tributyl phosphate.** Mariko Inarida (Chem. Dept., Fac. of Sci., Tokyo Univ., Hongo). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1958, **79** (6), 721–723.—After extraction of iodine with tributyl phosphate (**I**) from 0·2 *N* HCl in the presence of H_2O_2, both Te^{IV} and Te^{VI} remain in the aq. phase. By increasing the concn. of HCl to 4 *N*, Te^{IV} is extracted with **I** and Te^{VI} remains in the aq. phase. K. Saito

1312. **Colorimetric determination of iodate ion with 1-naphthylamine.** A. S. Vorob'ev. *Uch. Zap. Udmurtsk. Gos. Ped. Inst.*, 1957, (11), 150–154; *Ref. Zhur., Khim.*, 1958, (20), Abstr. No. 67,310.—A new colorimetric method is evolved for the determination of IO_3^- based on their reaction with 1-naphthylamine (**I**). It is considered that two processes take place, the oxidation of **I** by the IO_3^-, and halogenation of the oxidation product with the formation of 8-iodo-1:4-naphthaquinone, which is yellow. To determine IO_3^-, place in a colorimetric cylinder a known vol. of a 0·15% soln. of **I** (to 0·15 g of **I** add 75 ml of 96% ethanol and 25 ml of H_2SO_4, 2:1), add an equal vol. of 0·1 *N* KIO_3, mix, set aside for 10 min. and measure the extinction on a Duboscq colorimeter. The limit of detection of IO_3^- is 0·1 ml of 0·1 *N* KIO_3 or 0·35 mg of KIO_3, at a limiting dilution of 1 in $1·4 \times 10^4$. Interference is caused by the presence of BrO_3^-, CrO_4^{2-}, $Cr_2O_7^{2-}$, MnO_4^-, NO_2^-, BrO^-, ClO^- and IO^-; ClO_3^- and H_2O_2 do not interfere. C. D. Kopkin

1313. **Determination of radiochemical purity of iodine-131 and strontium-90 by paper electrophoresis.** M. Mach (Res. Inst. of Radiology, Prague). *Chem. Průmysl*, 1958, **8** (6), 303–305.—A method for the determination of systematic impurities in ^{131}I and ^{90}Sr has been worked out. When determining Te in ^{131}I, a preliminary oxidation to periodate and tellurate is necessary. The control samples had a radiochemical purity >99% in the case of ^{131}I and >99·9% in the case of ^{90}Sr. By combining paper electrophoresis with adsorption radiation analysis, the presence of ^{89}Sr in ^{90}Sr can also be detected. *Procedure for the oxidation*—To 0·25 ml of a soln. of the sample of ^{131}I add 0·015 ml of the carrier prepared by dissolving KI (13 g) and $NaHCO_3$ (0·01 g) in H_2O (1 litre). Then add NaClO (0·5 ml) (1·5 to 2% soln.) and heat for 15 min. on a water bath. J. Zýka

1314. **Amperometric titration of ferric iron with ascorbic acid and EDTA (disodium salt).** A. K. Zhdanov, V. A. Khadeev and A. L. Kats. *Uzb. Khim. Zhur.*, 1958, (1), 27–34; *Ref. Zhur., Khim.*, 1958, (20), Abstr. No. 67,292.—The amperometric titration is carried out with a platinum electrode in the form of a wire of length 8 mm and diam. 0·5 mm, rotating at 800 r.p.m. All measurements were carried out at zero potential of the platinum electrode *vs.* the S.C.E. A 0·1 *M* soln. of ascorbic acid (**I**) stabilised with formic acid or EDTA (disodium salt) (**II**) or a 0·1 *M* soln. of **II** was used for the titration. The titre of the soln. of **I** when kept in the dark at room temp. for 1 to 2 days is practically constant. The titration is effected by gradual increase of the sensitivity of the galvanometer as the reagent is added. Because of the polarisation of the electrode, the value of the max. deflection of the galvanometer needle was noted. In titrating with a soln. of **I**, the soln. being titrated may contain 0·28 to 1 mole of HCl per litre; with higher concn. of strong acid the oxidation of **I** is not limited to the formation of dehydroascorbic acid, and low results are obtained in determining Fe^{3+}. At the optimum concn. of HCl (0·5 mole per litre) the oxidation - reduction reaction takes place at the max. rate. Under these conditions the results of the determination of 1·5 to 18·7 mg of Fe^{3+} are reproducible and as a rule have an error ⩾1%. In titrating with **II**, satisfactory results are obtained if the soln. being analysed contains ⩾0·1 mole of HCl per litre. Small amounts of Fe (0·783 mg) may be titrated with high accuracy in an acetate buffer medium. In titrating Fe^{3+} in a medium 0·5 *M* in HCl, interference is caused by Ni^{2+}, Cu^{2+} and 10- or 20-fold amounts of Zn^{2+} or Cd^{2+}. No interference is caused by the presence of Mg^{2+}, Mn^{2+}, Co^{2+}, Cr^{3+}, Al^{3+}, Fe^{2+} or Ca^{2+}. The titration with **II** has been used for the determination of Fe^{3+} in dolomite. Titration with **II** has the advantages, as compared with titration with **I**, of rapidity of the determinations, the stability of soln. of **II**, and somewhat higher accuracy and sensitivity. On the other hand, the titration with **I** is more selective. C. D. Kopkin

1315. **Determination of iron (III) with tropolone and of tropolone with iron(III) and the formation constant of their complex.** Yoshinaga Oka and Shigeki Matsuo (Res. Inst. of Mineral Dressing and Metallurgy, Tohoku Univ., Nagamachi, Sendai). *Japan Analyst*, 1958, **7** (4), 215–219.—Ferric iron and tropolone (**I**) form two kinds of complex, green (max. absorption, 435 and 582 mμ) in the presence of an excess of Fe, and red - brown (425, 550 and

595 mμ) in the presence of an excess of **I**. The molar ratio of Fe to **I** appears to be 1:1 for the former and 1:3 for the latter complex. **I** ($<6 \times 10^{-4}$ *M*, >6 μg) is determined with Fe^{III} (in an amount 5 to 13 times the equiv. of the **I** in an acid soln., 0·05 to 0·5 *N* $HClO_4$ or 0·2 to 1 *N* HCl), and Fe^{III} (0·07 to 4 μg per ml) is determined with **I** (>30 times the equiv.) at pH ≃2. K. SAITO

1316. **Determination of ferrous oxide in chrome ores.** Hiroo Sasuga and Yoshio Iida (Inst. Technoanal. Chem., Fac. of Engng, Tokyo Univ., Hongo). *Japan Analyst*, 1958, **7** (4), 248–250.—The change in wt. of the sample ore during the oxidation ignition method (Shein, *Zavod. Lab.*, 1937, **6**, 505, 1199) was examined with a thermo-balance. When the content of Al and Mg is low, the increase in wt. on heating reaches a max at 800° to 900°, and the wt. then decreases at a higher temp. The temp. at which the wt. increase is recorded (general prescription, 1000°) must be changed according to the sample. By the use of V^{5+} in H_3PO_4 and H_2SO_4 for the oxidation of FeO, Cr^{3+} are partly oxidised. A blank test with the same amount of Cr^{3+} as that in the sample is indispensable. K. SAITO

1317. **Absorptiometric determination of iron in plutonium nitrate solutions (αα′-dipyridyl method).** U.K.A.E.A., Chem. Services Dept. (Operations Branch, Windscale, Cumb.). U.K.A.E.A. Report IGO-AM/W-183, 1958, 5 pp.—*Procedure*—A suitable vol. of the sample, containing 2 to 10 μg of Fe but <3 millimoles of HNO_3, is introduced into a 10-ml graduated centrifuge tube, and 4 ml of hydroxylamine hydrochloride - Na acetate reagent (100 ml of 25% Na acetate soln., 100 ml of 10% hydroxylamine hydrochloride soln., 10 ml of 1% 2:2′-dipyridyl soln. and 5 ml of 2% Na alkylsulphonate soln., shaken three times with 100 ml of $CHCl_3$) is added, followed by 0·2 ml of 1% 2:2′-dipyridyl soln. and 0·1 ml of 2% Na alkylsulphonate soln. The soln., now buffered at pH 3 to 6 and with the Fe present as Fe^{II}, is stirred for 1 min., 4 ml of $CHCl_3$ is added and the stirring is continued for 2 min. The liquid is centrifuged, and the $CHCl_3$ layer is withdrawn and combined with a further 4 ml of $CHCl_3$ from a second extraction. The extinction of the $CHCl_3$ soln., contained in a 4-cm glass Uvispek cell, is measured relative to that of $CHCl_3$ on a Spekker absorptiometer fitted with an Ilford 604 filter. A blank must be performed on the reagents. The work should be carried out in a glove box for sample soln. containing >1 mg of Pu. J. H. WATON

1318. **Absorptiometric determination of iron in uranium plant solutions and plant intermediates (αα′-dipyridyl method).** U.K.A.E.A., Chem. Services Dept. (Operations Branch, Windscale, Cumb.). U.K.A.E.A. Report IGO-AM/W-184, 1958, 6 pp.—Uranium plant intermediates are converted into soln. of $UO_2(NO_3)_2$. Uranium tetrafluoride (≃0·7 g) is hydrolysed to black uranium oxide with steam in a furnace at 500° ± 50°, and this and other uranium oxides (≃0·6 g) or $(NH_4)_2U_2O_7$ (≃0·65 g of dried sample) are dissolved in 1·5 ml of 8 *M* HNO_3. The soln. are diluted to 5 ml and suitable aliquots containing 2 to 10 μg of Fe but ⩾ 0·05 g of U are introduced into a 10-ml graduated centrifuge tube. The determination is carried out exactly as described previously (*cf. Anal. Abstr.*, 1959, **6**, 1317). J. H. WATON

1319. **New colour reactions for ferricyanides.** N. S. Frumina (Saratovsk State Univ.). *Zhur. Anal. Khim.*, 1958, **13** (5), 586–589.—The colour reactions of ferricyanide ion with a number of diphenylaminecarboxylic acids are studied. The most sensitive are (with colour formed and sensitivity in μg per ml) *o′*-methoxyphenylanthranilic acid (red, 23·0), *o′*-nitrophenylanthranilic acid (**I**) (yellow - brown, 1·0), diphenylbenzidine-*oo′*-dicarboxylic acid (**II**) (red - brown, 2·3) and diphenyltolidine-*oo′*-dicarboxylic acid (**III**) (red - brown, 0·5). The products obtained when using **I**, **II** and **III** have max. absorption at 470 mμ. C. D. KOPKIN

1320. **Use of diphenylcarbazone for the photometric determination of copper in iron and steel.** L. N. Lapin and N. V. Reis (Samarkand Med. Inst.). *Zhur. Anal. Khim.*, 1958, **13** (4), 426–429.—The copper derivative of diphenylcarbazone is insoluble in water but is extractable with benzene and its homologues, and the intensity of the red colour obeys the Beer - Lambert law. The reaction is specific, highly sensitive, and permits detection of tenths parts of a microgram of Cu. The experimental error is ⩾4%. *Procedure*— Take 2 ml of an acid soln. and add 0·2 g of KH_2PO_4, and phenolphthalein soln. Add twice the volume of aq. NH_3, then neutralise the soln. with a saturated soln. of KH_2PO_4 added dropwise. Add water to ≃15 ml. To the soln. add 5 ml of a benzene soln. of diphenylcarbazone, shake well for 1 min., and measure the extinction of the benzene soln. in an absorptiometer. As a blank use the soln. of diphenylcarbazone in benzene. Prepare a calibration curve from known amounts of Cu. W. ROUBO

1321. **Determination of boron in high-alloy steels.** Shigeo Wakamatsu (Toto Seiko Co., Minamisunamachi, Koto-ku, Tokyo). *Japan Analyst*, 1958, **7** (6), 372–376.—The decomposition of a high-alloy steel and the determination of B by a modified Chapin method were examined. Since methyl borate is quant. distilled from conc. H_2SO_4 - H_3PO_4 soln. in a current of air, the sample is decomposed with any acid except HF. The distillate is absorbed in NaOH and determined colorimetrically with carmine (**I**) in conc. H_2SO_4. The time taken for an estimation is >1·5 hr. *Procedure*—Dissolve the sample (0·5 g) in 10 ml of acid (*e.g.*, aqua regia or a mixture of HCl, HNO_3, H_2SO_4 and H_3PO_4), transfer the product to a distilling flask, add H_2SO_4 and H_3PO_4 to make the sum of each acid 5 ml, and heat to white fumes. Metal nitride or carbide is decomposed by this procedure. Add methanol (20 ml) and distil into 0·1 *N* NaOH (5 ml) at 100° to 150° (bath temp.) in a slow current of air. Keep the absorbing liquor alkaline with occasional addition of NaOH. Cool, add methanol (10 ml) and continue the distillation until white fumes appear in the flask. Evaporate the distillate to dryness and heat the residue at 70° for 1 hr. with H_2SO_4 (15 ml) and **I** (0·05% in H_2SO_4) (1 ml). Measure the extinction at 600 mμ. Prepare a standard series (<50 μg of B) from sodium tetraborate soln. K. SAITO

1322. **A rapid spectral method for the determination of trace elements in ferrosilicon.** O. Bělohlávek (SONP, Kladno, Czechoslovakia). *Hutn. Listy*, 1958, **13** (5), 426–428.—A rotating carbon electrode has been used for the spectral determination of Al, Mn, Ti, Cu and Ni in all types of ferrosilicon. J. ZÝKA

1323. **Investigations on colorimetric methods of metallurgical analysis. VI. Estimation of silicon in cast iron using the Duboscq type of colorimeter.** G. V. L. N. Murty. *Metallurgia, Manchr*, 1958, **58**, 52–54.—A description is given of a simplified procedure requiring only 15 min. for a single determination. J. W. O. PYEMONT

1324. **Colorimetric determination of titanium in steel.** M. Novotný (Závod Přesného Strojírenství, Gottwaldov, Czechoslovakia). *Hutn. Listy*, 1958, **13** (5), 430–431.—If EDTA (disodium salt) is added to a soln. of steel containing (in addition to Ti) W, Mo, Cr, Ni, Fe, Al and V, the interfering elements can be masked; after addition of a magnesium salt, Ti is set free from the weak complex and can be pptd. with aq. NH_3 and determined colorimetrically with H_2O_2. *Procedure*—Dissolve the sample (1 g) in a mixture of HCl and HNO_3 by heating. Add $HClO_4$ (75%) (30 ml) and heat till Cr^{III} is converted into $Cr_2O_7^{2-}$. Cool, add H_2O (200 ml) and a soln. of EDTA (disodium salt) (10%) (70 ml), neutralise with aq. NH_3 (litmus), add aq. NH_3 in excess (5 ml) and $MgSO_4$ soln. (10%) (30 ml). Set aside for 1 hr., then filter off the ppt. and wash it with dilute aq. NH_3. Transfer the ppt. to a 200-ml flask and dissolve it in hot H_2SO_4 (1:3) (50 ml); add H_3PO_4 (5 ml), cool, and dilute to vol. with H_2O. To 100 ml of the soln. add H_2O_2 (15%) (5 ml) and measure the extinction with the use of Hg 436 filter. Compare with a calibration curve. Results are accurate to within $\pm 2\%$. J. ZÝKA

1325. **Enhanced precision in the quantometric determination of phosphorus in low-alloyed steels.** N. Lounamaa (Fagersta Bruks AB, Sweden). *Appl. Spectroscopy*, 1958, **12** (2), 53–54.—The use of a fixed integration time, combined with the calculation of the ratio of the P line 2149·1 A, with its associated background, to the internal standard Fe 2714·4 A, was found to give improved precision. Phosphorus contents in the range 0·01 to 0·07% were determined with a coeff. of variation of $\simeq 3\%$ compared with $\simeq 9\%$ obtained by the normal integration method. P. T. BEALE

1326. **Determination of vanadium in steel with the use of aluminon.** I. S. Mustafin and E. A. Kashkovskaya (N. G. Chernyshevsky Saratov State Univ.). *Zhur. Anal. Khim.*, 1958, **13** (2), 215–218.—Vanadium in steel can be determined colorimetrically with aluminon, measuring the extinction at 530 mμ. Interference is caused by Al, Cu^{2+}, Be^{2+}, Th^{4+}, Ce^{3+}, Ti^{4+} or UO_2^{2+}. Thioglycollic acid is used to prevent interference by Fe^{3+} and Cr^{3+}. W. ROUBO

1327. **The stylometric analytical method applied to foundry and raw materials.** E. Cazacu and P. Tudor. *Rev. Chim., Bucharest*, 1958, **9** (6), 320–322.—The method is based on the use of the sample as one of the electrodes for spectral analysis while the other consists of technically pure iron, or copper for non-ferrous alloys. A spectral line in the spectrum of the element to be estimated is chosen which is near a line in the spectrum of the metal used for comparison. The intensities of these spectral lines are first measured on the pure substances, and the analysis consists in comparing the intensity of the chosen line of the element with that of the reference element. The difference in intensity of this pair of lines compared with the original pair unadulterated is a direct function of the concn. of the element being sought. These differences are measured photometrically and compared with standard curves. The pair of lines chosen must fulfil the following conditions—the relation between their intensities must not be sensitive to variations in the conditions of excitation; they must both be in the same field of vision of the apparatus, but their wavelength difference must be < 5 A; they must have the appropriate ionisation potentials; they should not be diffused; at the mean concn. of the element sought, the lines must be able to be brought to equal intensity within the limits of the instrument. H. SHER

1328. **Phase analysis of iron ores. III. Selective dissolution of magnetite in the presence of haematite.** N. Kh. Pinchuk and Yu. V. Morachevskiĭ. *Vestn. Leningr. Univ.*, 1958, (4), 126–133; *Ref. Zhur., Khim.*, 1958, (20), Abstr. No. 67,314.—The dissolution of magnetite (**I**) and haematite (**II**) is studied, in order to find the conditions for the selective dissolution of **I**. The study is based on a finding that the selective dissolution of **I** with H_3PO_4 from a mixture of **I** and **II** is possible only if the Fe^{II} of **I** is oxidised in soln. to Fe^{III} with permanganate. The interference of Fe^{II} may therefore be removed by addition of an oxidant ($KMnO_4$, H_2O_2) or a complexing reagent. (For Part II see Morachevskiĭ and Pinchuk, *Anal. Abstr.*, 1958, **5**, 520.) C. D. KOPKIN

1329. **Photometric determination of cobalt as cobaltinitrite.** F. Modreanu and N. Iorga (Inst. of Chem., Iaşi Filial, Acad. Sci., Iaşi, Romania). *Zhur. Anal. Khim.*, 1958, **13** (5), 617–618.—To a soln. of Co^{2+} containing 0·35 to 1·50 mg per ml (1 ml) add glacial acetic acid (2 ml) and a soln. of chemically pure $NaNO_2$ (120 g dissolved in 180 ml of twice-distilled water) (5 ml). Pass air through the soln. for 10 to 15 min. to remove oxides of N and make up to 25 ml (pH $3·9 \pm 0·1$). Measure the extinction in a 10-mm cell with a blue filter, with water as comparison soln. A calibration curve is constructed by using various amounts of a standard soln. of Co^{2+} containing 0·5 mg per ml. Beer's law is obeyed in the concn. range indicated. Even trace amounts of K^+ and NH_4^+ cause interference. Up to 1 mg of Fe^{3+} may be masked by adding NaF but larger amounts of Fe^{3+} interfere. Up to 1 mg of Cr^{3+} has practically no influence on the optical density of the soln. Up to 2 mg of Sn^{2+} does not interfere, but larger amounts form a gelatinous ppt. The presence of Cu^{2+}, Bi^{3+} or VO_3^- also causes interference. No interference is caused by 10 mg of Pb^{2+} or Sb^V, 20 mg of Zn^{2+}, Cd^{2+} or Mn^{2+}, or 24 mg of Ni^{2+}. Large amounts of U^{VI} do not interfere. C. D. KOPKIN

1330. **Cathodic electro-deposition methods for cobalt.** D. Salyer and T. R. Sweet (McPherson Chem. Lab., Ohio State Univ., Columbus 10, U.S.A.). *Anal. Chem.*, 1958, **30** (10), 1632–1635.—Cobalt (50 to 60 mg) was deposited under 10 commonly used sets of conditions. A total of 43 determinations was made. The Co^{2+} content of electrolyte and washings was determined radiochemically by addition of ^{60}Co to the original soln. It is shown that all the methods studied give results that are high (average 0·74 mg) even without correcting for the Co removed from the deposit on washing (average 0·45 mg). When the electrodes are removed from the soln. without being washed and without switching off the current no Co^{2+} can be detected in the electrolyte. Examination

of washings of the electrodes showed losses of Co of 0·1 to 0·25 mg. T. R. ANDREW

1331. **Rapid method for the determination of cobalt and iron in the catalyst for the synthesis of hydrocarbons from water gas.** Yu. L. Polyakin. *Trudy Groznensk. Neft. Inst.*, 1958, (20), 24–32; *Ref. Zhur., Khim.*, 1958, (20), Abstr. No. 67,295.—The method described for the determination of the ratio Fe:Co is based on dissolution of the sample of catalyst in conc. HCl, with subsequent photometry of the chloride complex of Co with a red filter, and of the chloride complex of Fe with a blue or violet filter. The determinations take 10 min.; the error is ±10%. C. D. KOPKIN

1332. **Rubeanic acid [dithio-oxamide] and derivatives as colorimetric reagents. I. Spectrophotometric determination of cobalt, nickel, palladium, silver and ruthenium with rubeanic acid.** J. Xavier and Priyadaranjan Rây (Indian Ass. for the Cultivation of Sci., Calcutta). *J. Indian Chem. Soc.*, 1958, **35** (6), 432–444.—Cobalt, Ni and Pd are determined in ethanolic pyridine soln. Cobalt is determined in the presence of Cu, Ni and Ag with KCN and thiourea as masking agents; and Ni is determined in the presence of Cu and Ag with thiourea as masking agent. An extraction procedure for Pd with *iso*amyl alcohol, with EDTA (disodium salt) as sequestering agent, is described. Silver is determined in aq. medium at pH 4·0 to 4·6. The method for the determination of Ru (*cf.* Ayres and Young, *Anal. Chem.*, 1950, **22**, 1281) is modified and improved. The colour system in all cases obeys Beer's law and gives values of high sensitivity. I. JONES

1333. **Examination of the spectrophotometric determination of nickel by the extraction of its dimethylglyoxime complex with chloroform.** Hiroshi Kitagawa and Norio Shibata (Hitachi Central Res. Lab., Kokubunji, Tokyo). *Japan Analyst*, 1958, **7** (5), 284–287.—When the dimethylglyoxime complex of Ni is extracted with $CHCl_3$ at pH 5 to 9, Cu (>0·4 mg), Fe (>500 mg) and Cr (>20 mg) cause interference. Copper is extracted back with an ammonium acetate buffer of pH 8·5 containing 1% dimethylglyoxime in ethanol (1 ml per 20 ml). No interference results from Bi, Cd, Mo, Sn, Sb, V, W, Zn (<500 mg each) or Mn (<100 mg). K. SAITO

1334. **Photometric determination of sulphur in metallic nickel by the methylene blue method.** Shigeru Yokosuka and Shoichi Shirakawa (Bessi Mine Office, Sumitomo Mining Co., Niihama, Ehime-ken). *Japan Analyst*, 1958, **7** (6), 368–372.—Sulphur (<0·003%) in metallic nickel is distilled in a current of N as H_2S by St. Lorant's method (*Z. physiol. Chem.*, 1929, **185**, 245; Johnson and Nishita, *Anal. Chem.*, 1952, **24**, 736), and then absorbed in Zn acetate and colorimetrically determined by the methylene blue method (*cf.* Fogo, *Anal. Chem.*, 1949, **21**, 732). The experimental conditions were examined. No interference results from Cu, Pb, Bi, Sb^{III}, Sn^{IV}, As^{III}, Zn, Fe^{III}, Mn, Al or Co; Se and Te must be removed as bromide. The error is ≃10%. *Procedure*—Dissolve the sample (1 g) in HNO_3 (1 + 1, 10 ml), evaporate to dryness with HCl several times, transfer to a distilling flask and heat to a syrupy soln. Add water (2 ml) and 5 ml of the reducing agent [a mixture of HI (sp. gr. 1·70, 100 ml), formic acid (85%, 80 ml) and red phosphorus (15 g) is heated at 115° for 1·5 hr. in a current of N] and boil for 1 hr. in a current of N, allowing the liberated H_2S to pass into 35 ml of Zn acetate soln., pH >5. Cool this soln., mix with *p*-aminodimethylaniline sulphate (0·2% in 12 *N* HCl) (5 ml) and then with $FeCl_3$ (10%, 1 ml), make up to 50 ml and measure the extinction at 665 mμ after 15 min. K. SAITO

1335. **Determination of traces of noble metals in rocks.** P. Hahn-Weinheimer (Mineral. Inst. der Univ., Frankfurt/M.). *Z. anal. Chem.*, 1958, **162** (3), 161–167.—A method is described for the preparation of quinoline-2-selenol (**I**) which is a very sensitive reagent for the pptn. of the noble metals. To determine sub-micro quantities of the noble metals in rocks, prepare an extract, acidify, reduce with hydroxylamine hydrochloride, add a soln. of **I** in 8 *N* HCl and extract with $CHCl_3$; evaporate the $CHCl_3$ extract to dryness and submit the residue to emission spectrography. The limits of detection are: Os^{IV} 2 μg; Ir^{III}, Ru^{III} and Rh^{III} 0·05 μg; Pt^{IV} and Pd^{II} 0·01 μg. A. R. ROGERS

1336. **Separation of the platinum metals by ion exchange.** S. S. Berman and W. A. E. McBryde (Univ. of Toronto, Ontario, Canada). *Canad. J. Chem.*, 1958, **36** (5), 835–844.—The separation and elution of various combinations of Rh, Ru, Ir^{III}, Ir^{IV}, Pd^{II} and Pt^{IV}, in the form of their chlorides, on a column of Amberlite IRA-400 (100 mesh) is discussed. P. M. SORGO

1337. **Separation of rhodium and iridium by ion exchange.** S. S. Berman and W. A. E. McBryde (Univ. of Toronto, Ontario, Canada). *Canad. J. Chem.*, 1958, **36** (5), 845–852.—A column of Amberlite IRA-400 (70 to 100 mesh) is used. The resin is washed with 10 ml of water, then with 10 ml of a Ce^{IV} soln. (**I**) [add 1 ml of 0·1 *M* $Ce(SO_4)_2$ to 100 ml of 0·8 *M* HCl]. Rhodium and Ir, as their chlorides, are fed on to the column and Rh is eluted by **I**. Iridium remains on the column as Ir^{IV}, and is removed by Soxhlet extraction with 6 *M* HCl. Recoveries of 100% are achieved. P. M. SORGO

1338. **Analytical application of 8-mercaptoquinoline (thio-oxine) and its derivatives. II. Photometric determination of small amounts of palladium.** Yu. A. Bankovskii and A. F. Ievin'sh (Inst. Chem., Acad. of Sci., Latvian SSR, Riga). *Zhur. Anal. Khim.*, 1958, **13** (5), 507–512.—To the soln. to be analysed (≯ 25 ml) add an equal vol. of conc. HCl, an 8% soln. of thiourea (1·5 ml) (to complex with Os, Ru, Pt, Cu, Ag, Au, and Hg) and a 4 to 5% soln. of thio-oxine in 6 *N* HCl (5 ml). Extract the Pd complex by vigorous shaking with 10 ml of $CHCl_3$ for 5 min. Separate the $CHCl_3$ layer, filter it through cotton wool and measure the extinction in a 1-cm cell at 485 mμ. Determine the Pd from a calibration curve. Beer's law is obeyed up to 27 μg of Pd per ml. The absorption spectrum of the Pd complex in $CHCl_3$ has max. at 272, 286 and 485 mμ. No interference is caused by Fe^{3+} (up to 80 mg) in 6 *N* HCl; larger amounts (up to 200 mg) may be reduced with sodium hypophosphite. When present in amounts >20 μg, Mo produces a brown colour in the $CHCl_3$ layer; this is removed by shaking once or twice with 60 ml of 8 *N* HCl and filtering. No interference is caused by the presence of Al, Ti, Zr, Hf, Th, Cr and other elements which do not form sulphides stable in water, Ir, Se, Co, Ni, Zn, Cd, Pb, Mn, Tl, Sn, W, Sb, Bi, U, As or Ge, even when present in amount large compared with that of Pd. C. D. KOPKIN

1339. **Determination of calcium, magnesium, aluminium, silicon and tin in refined platinum and palladium.** S. A. Borovik, A. V. Babaeva, N. I. Ushakova and R. I. Rudȳī (N. S. Kurnakov Inst. of Gen. and Inorg. Chem., Acad. Sci., USSR, Moscow). *Zhur. Anal. Khim.*, 1958, **13** (5), 580–582.—Directions are given for the preparation of standards. A 1% soln. of Pt was prepared from twice-recrystallised *cis*dinitrodichlorodiamminoplatinum; this still contained 0·002% of Ca, determined by extrapolation of the calibration curve. Soln. were prepared containing 0·5% of Pt and 0·0001, 0·0003, 0·001, 0·003 and 0·01% of the elements to be determined. The spectra were photographed on a Hilger spectrograph in an a.c. arc, from the pairs of lines Ca II 3933·67 and Pt I 3966·36, Mg II 2802·7 and Pt I 2803·24, Al I 3961·52 and Pt I 3966·36, Si I 2881·58 and Pt I 2893·87, and Sn I 3034·12 and Pt I 3036·43 A. Correction was made for the background. From the calibration curves, up to 0·002% of Ca and up to 0·02% of Mg and Al may be determined with a mean error of ±6%, and up to 0·02% of Si and up to 0·06% of Sn may be determined with a mean error of ±9%. Standard soln. of Pd were prepared similarly. The dichlorodiamminopalladium starting material contained 0·001% of Ca and 0·0005% of Mg (found by extrapolation) after fivefold recrystallisation. It was reduced in H and dissolved in aqua regia (the HNO_3 and HCl being first distilled in quartz apparatus), the HNO_3 then being removed by carefully boiling with conc. HCl. The soln was diluted and then evaporated to a small vol. and made up to a standard vol. The spectrographic soln. contained 0·5 and 1% of Pd and from 0·2 to 0·006% of Ca, Mg, Al and Sn, and from 0·1 to 0·0003% of Si, relative to Pd. The pairs of lines used were Ca II 3933·67 and Pd I 3958·64, Pd I 3922·96, Mg I 2852·13 and Pd II 2854·58, Al I 3961·52 and Pd I 3958·64, Sn I 3034·12 and Pd II 3032·08, and Si 2881·58 A against the background. In the case of the 1% soln. of Pd, which gives very intense lines, 0·1% of Pt was added as internal standard. The sensitivity of the determinations in the soln. of Pt and Pd reached 10^{-5} % of Ca, 3×10^{-5} % of Mg, 10^{-4} % of Al and Si, and 3×10^{-4} % of Sn. C. D. KOPKIN

1340. **Method for determining un-ignited acid-insoluble residue of carbonate rocks.** R. R. Thompson (Coll. Mineral Industries, Pennsylvania State Univ.). *Bull. Min. Ind. Exp. Sta.*, 1958, (71), 15–18.—A wet chemical method has the advantage over the normal method, involving the determination of ignited acid-insoluble impurities, of leaving a residue suitable for further microscopic examination and of being more rapid. *Procedure*—Dissolve the sample (10 g) in HCl (1:1) (100 ml) and allow the beaker to stand on a hot-plate at 75° to 80° for 2 to 3 hr. Decant and add a further 15 ml of HCl (1:1) to ensure complete solution, centrifuge for 10 min., decant and add water (5 ml), repeating this operation twice. Loosen the residue by mixing with an air jet, pour the sample into a porcelain dish and evaporate to dryness. R. A. HOWIE

1341. **Analysis of rutile - anatase mixtures by measurement of dielectric constants.** F. Oehme (Lab. der Wiss.-Tech. Werkstätten, Weilheim/Obb, Germany). *Farbe u. Lack*, 1958, **64**, 319–321.—The immersion dielectric constants of pure rutile and anatase TiO_2 have been found to be 80 and 46, respectively. For the analysis of mixtures, acetone is used as the immersion liquid, and the composition is derived from a calibration curve prepared from known mixtures. L. A. O'NEILL

1342. **Fluoride analysis of glasses and silicate materials by pyrohydrolysis separation.** P. B. Adams and J. P. Williams (Corning Glass Works, New York, U.S.A.). *J. Amer. Ceram. Soc.*, 1958, **41** (9), 377–380.—Pyrohydrolysis is accomplished by passing steam over a mixture of sample and U_3O_8 at a temp. of ≃1000°; 30 min. is sufficient except for samples containing appreciable amounts of Ca. Silica-glass tubing (96%) is substituted for nickel in the apparatus described by Susano *et al.* (*Anal. Abstr.*, 1955, **2**, 2414). Interferences are negligible with this method. The entire determination can be completed in ≃1 hr. The results are generally slightly higher than those obtained by conventional methods of separation, indicating better fluoride recovery. The average reproducibility is ±2% relative. K. R. C.

See also Abstracts—**1177**, EDTA in metallurgical analysis. **1179**, Colorimetric reagent for Ni and Cu. **1180**, Reactions of *p*-dimethylaminobenzylidenerhodanine with metal ions. **1181**, Polarographic behaviour of tetraphenylstibonium chloride with metal ions. **1419**, Co-pptn. of Ag with Te. **1423**, Determination of Zn. **1432**, Determination of Po in urine. **1563**, Determination of Ni in soils and rocks. **1564**, Determination of clay minerals by X-ray diffraction. **1592**, Emission micro-X-ray spectrography of metals.

3.—ORGANIC ANALYSIS

Determination of elements and radicals and of organic compounds not included in other sections. Organic industrial products, including petroleum and its products, fuels, detergents, volatile oils, cosmetics, dyestuffs, fibres, plastics, resins, paints, elastomers, leather, explosives.

1343. **Analysis for industry.** J. Körbl (Czech. Acad. Sci., Prague). *Ind. Chem. Mfr*, 1958, **34**, 563–566.—A review is presented of some 116 modern or recently developed methods for the micro- or semi-micro determination of the following elements in organic compounds—O, N, S, Cl, Br, I, F, As, Sb, Si and metals. H. L. WHITEHEAD

1344. **Analysis for industry. Recent developments in methods for the micro-determination of carbon and hydrogen.** J. Körbl (Czech. Acad. Sci., Prague). *Ind. Chem. Mfr*, 1958, **34**, 507–510.—A review is presented of recent literature on micro-analytical methods for determining C and H in organic compounds by either the empty-tube or catalytic procedures of combustion in a current of O. (77 references.) W. J. BAKER

1345. **Determination of nitrogen by the strong phosphoric acid and the Dumas method. Information obtained by mass spectrometry.** Shigeru Ohashi, Yuzi Takayama, Sachiko Taki and Hiroshi Toya (Fac. of Sci., Kanazawa Univ., Kanazawa). *Japan Analyst*, 1958, **7** (4), 205–210.—The gas in the nitrometer, collected by Ohashi's strong phosphoric acid - iodic acid method (*cf. Anal. Abstr.*, 1955, **2**, 2448) or by the Dumas method was submitted to mass spectrometry. The gas always consists of N_2 and N_2O, the ratio N_2 to N_2O varying according

to the conditions, but the amount of N_2O obtained by the former method is significantly greater than that by the latter. Pyridine rings are not decomposed by the former method at $< 240°$, but are completely decomposed at 250°, at which temp. HIO_3 decomposes with evolution of O. Since N_2O dissolves in conc. KOH soln. only very slowly, its presence does not cause interference. K. SAITO

1346. **A new method for determination of nitrogen and halogens or nitrogen, sulphur and halogens in a single sample of an organic substance.** P. N. Fedoseev and N. P. Ivashova (S. O. Makarov Shipbuilding Inst., Nikolaev). *Zhur. Anal. Khim.*, 1958, **13** (2), 230–234.—Nitrogen, sulphur and halogens are determined by heating with magnesium powder at 550° to 650° in the absence of air which is expelled by means of diethyl ether. The product is heated with dil. H_2SO_4, made alkaline and the NH_3 distilled into 0·1 *N* $KIO_3.HIO_3$ soln. When distillation is complete, KI soln. is added and the iodine is titrated. The liquid in the distillation flask is again acidified with H_2SO_4 and the halogen is titrated with $AgNO_3$. If S is present, the H_2S is distilled from acid soln. before the NH_3, and determined iodimetrically.

W. ROUBO

1347. **New methods for the quantitative determination of halogens in organic substances. II. Gravimetric determinations of chlorine, bromine and iodine.** P. N. Fedoseev and M. Ya. Sobko (S. O. Makarov Shipbuilding Inst., Nikolaev). *Zhur. Anal. Khim.*, 1958, **13** (5), 595–598.—Ignite the substance, covered with a layer of quartz sand or chromium oxide, in a current of air or O, increasing the temp. slowly up to 750° or 800°. Pass the resulting gases, containing the halogens, through a tube heated at 800° to 900°, and then through a tube containing KBr or NaBr heated at 650° to 680°, a tube containing KI at 450° to 500°, a tube containing moist KI at room temp., and finally through a Winkler tube containing 10% KI soln. Free Cl oxidises Br^- in the bromide tube, free Br oxidises I^- in the iodide tube, and free iodine is absorbed by the moist KI, any passing through being trapped in the Winkler tube. By measuring the changes in weights of the bromide and iodide tubes and by titrating free iodine in the moist KI tube and the Winkler tube taken together, the Cl, Br and I content of the organic substance may be determined. The analysis takes 40 to 50 min. The error of the determination is $\gtrsim \pm 0{\cdot}2\%$. The presence of S causes interference. The method is simple and reliable. (For Part I see *Anal. Abstr.*, 1956, **3**, 1352.)

C. D. KOPKIN

1348. **Improvement of the silver-gauze method for the determination of chlorine and bromine in organic compounds.** Masao Kunori (Kita College, Tohoku Univ., Kitashichi-bancho, Sendai). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1958, **79** (6), 773–774.—The method is significantly improved by the following two modifications. The sample (5 to 10 mg) is oxidised with a mixture of Ag_2CrO_4 and K_2CrO_4 (1 + 1, by wt.) (0·5 g) with the addition of H_2SO_4 (2 ml) (Zacherl *et al.*, *Mikrochem.*, 1932, **11**, 61). The silver gauze is weighed in the absorbing tube, which has narrow inlet and outlet tubings, without being transferred into a weighing bottle.

K. SAITO

1349. **Organic elementary analysis with a micro-bomb. IV. Separation and micro-determination of chlorine and bromine in an organic compound by ion-exchange chromatography.** Asaji Kondo (Lab. of Org. Chem., Tokyo Inst. of Tech., Meguro-ku, Tokyo). *Japan Analyst*, 1958, **7** (4), 232–234.—The ion-exchange separation of Cl^- and Br^- by Dowex 1-X10 (NO_3) (DeGeiso *et al.*, *Anal. Abstr.*, 1955, **2**, 924) was applied to org. elementary analysis. The sample (10 mg) is decomposed with Na_2O_2 in a micro-bomb (Kondo, *Anal. Abstr.*, 1958, **5**, 548, 2664), treated with HNO_3 and water, and evaporated to produce $\simeq 8$ ml of neutral $NaNO_3$ soln. (< 3 *M*). The product is passed through the column (100 to 200 mesh, 3 sq. cm × 10 cm), which is successively eluted with 0·5 *M* (70 ml) and 2·0 *M* (70 ml) $NaNO_3$ to collect Cl^- and Br^-, respectively. The error is $< 0{\cdot}5\%$. K. SAITO

1350. **Determination of primary, secondary and tertiary amino groups when present together.** G. D. Gal'pern and N. N. Bezinger (Inst. of Petroleum, Acad. Sci., USSR, Moscow). *Zhur. Anal. Khim.*, 1958, **13** (5), 603–607.—Dissolve the sample in glacial acetic acid. Titrate an aliquot potentiometrically with a 0·05 or 0·1 *N* soln. of $HClO_4$ in glacial acetic acid to determine the total amino groups. To another aliquot add 1 g of phthalic anhydride and heat under reflux on a boiling-water bath for 30 to 45 min. Cool and titrate the total secondary and primary amino groups, which remain unacylated. To a third aliquot add 10 or 15 ml of acetic anhydride and heat under reflux on a boiling-water bath for 30 to 45 min., cool, and titrate the tertiary amino groups, which are not acetylated. The amounts of primary, secondary and tertiary amino groups may then be calculated.

C. D. KOPKIN

1351. **Determination of acetylene from carbide.** O. Frehden and M. Beclereanu. *Rev. Chim., Bucharest*, 1958, **9** (6), 333–334.—The principle of the proposed method is the reaction of the C_2H_2 liberated by the action of H_2O on the carbide with $AgNO_3$, and titration of the HNO_3 liberated with NaOH. *Procedure*— Approx. 2 g of carbide is suspended in the neck of a special distillation flask containing 100 ml of H_2O and fitted with a hollow cooled stopper. The vapour from the boiling H_2O condenses on the cooled stopper and drips into the carbide. The C_2H_2 liberated passes into a neutral soln. of 100 ml of H_2O, 10 g of $AgNO_3$, 10 ml of acetone and 2 or 3 drops of methyl red. Titration with *N* NaOH follows the colour change of the indicator, and after distillation for 10 to 15 min., the cooling of the stopper is ended. Distillation is continued until the indicator no longer reverts to red after one drop of NaOH soln. H. SHER

1352. **Use of adsorption methods of analysis and the separation of gaseous hydrocarbons in kinetic studies by the use of labelled atoms.** A. I. Brodskiĭ, R. A. Kalinenko and K. P. Lavrovskiĭ. *Problemy Kinetiki i Kataliza*, 1957, **9**, 399–404; *Ref. Zhur., Khim.*, 1958, (19), Abstr. No. 64,256.—A gas analyser (*Ref. Zhur., Khim.*, 1957, Abstr. No. 16,706) is described, with four columns containing, respectively, silica gel, activated carbon, pumice-stone saturated with tri*iso*butylene, and pumice-stone saturated with acetonylacetone. The carrier gas is CO_2; after passage through the columns the CO_2 is adsorbed on activated carbon at the temp. of liquid N, on ascarite or with KOH soln. The course of the separation of the gases is followed by a membrane manometer. Chromatograms are given of the separation of multi-component mixtures

of gases not condensible at the temp. of liquid N, *i.e.*, H, air and saturated and unsaturated hydrocarbons up to C_4, inclusive. The apparatus is used successfully for the analysis of mixtures of gases from cracking processes containing up to 12 components. The isomers of butylene and butadiene are not separated. The analysis takes 3 to 5 hr. In the separation of CH_4 labelled with ^{14}C from C_2H_6 and C_2H_4 the latter components when separated show no activity. The accuracy of the analysis is within 0·5 to 1% abs. With a concn. of separate components of $<1\%$, the relative accuracy is $\simeq 30\%$. The lower limit of sensitivity of the apparatus is $\simeq 0{\cdot}1\%$. C. D. KOPKIN

1353. **Methanol.** British Standards Institution. (2, Park St., London). B.S.506:1958, 13 pp.—Limits are specified for maximum sp. gr. at 15·5°, 20° and 25°, apparatus and methods of determination are specified, and standards are laid down for distillation range, residue on evaporation, miscibility with water, acidity, aldehydes and ketones, and sulphur and sulphur compounds. The amount of sample to be taken from the bulk, and the conditions of storage are specified. R. E. ESSERY

1354. **Measurement of the ethanol content of liquids containing dissolved substances.** J. Krutzsch. *Dtsch. ApothZtg*, 1958, **98** (25), 609–610.—An apparatus is described for the estimation of the ethanol content of tinctures, wines, etc. The liquid is heated by an electric lamp and the difference between the initial and final temp. for a specified expansion of the liquid is noted. The difference indicates the ethanol content, as the expansion increases considerably with addition of ethanol. The apparatus can also be used to measure the specific expansion of other liquids.
M. H. SAWISTOWSKA

1355. **Colour reactions of alcohols and ketones with Schiff's reagent.** L. Rosenthaler (Seftigenstrasse 40, Bern, Switzerland). *Mitt. Lebensmitt. Hyg., Bern*, 1958, **49** (4), 237–239.—The sensitivity of the reagent and its specificity were found to depend on the mode of preparation of the reagent and the manufacture of the fuchsine. False positives were obtained if the time interval between addition and reading was prolonged. Three reagents containing fuchsines of various makes and crystallinity were compared. The reagent containing "Merck" crystalline fuchsine showed the greatest specificity for aldehydes. S. BAAR

1356. **Separation of glycerol from a polyhydric alcohol mixture by non-ionic exclusion.** I. T. Clark (Forest Products Lab., U.S. Dept. of Agric., Madison, Wis.). *Anal. Chem.*, 1958, **30** (10), 1676–1678.—For satisfactory separation of glycerol from other polyhydric alcohols, apply the sample (30 ml) to a column of Dowex 50-X12 resin (H^+ form) (1 litre) at 60° and elute with preheated H_2O at a flow rate of 2 ml per min. (*cf.* Wheaton and Baumann, *Ann. N.Y. Acad. Sci.*, 1953, **57**, 159).
A. R. ROGERS

1357. **Determination of the degree of substitution of carboxymethylcellulose (CMC), using radioactive salts.** C. Simionescu and N. Asandei (Scoala Polytech., Iaşi, Romania). *Chim. Anal.*, 1958, **40** (6), 204–206.—By pptn. of the thorium or, preferably, the uranyl, salts of the cellulose glycollic acid, followed by a count of the α-activity, it is possible to determine the degree of substitution of carboxymethylcellulose both rapidly and accurately. The results are calculated both by the formula proposed by Francis (*cf. Anal. Chem.*, 1953, **25**, 941) and by a new formula. The cellulose glycollic acid is found to have a degree of substitution ranging from 0·2 to 1·2 for the monomeric form. The method described is precise, but the results are somewhat lower than those given by a volumetric method, in which other factors may cause errors. J. H. WATON

1358. **Studies on detection, characterisation and determination of aldehydes. III.** S. Veibel, I. G. K. Andersen and B. J. Nielsen (Univ. Tech., Copenhagen, Denmark). *Suomen Kem., B*, 1958, **31** (1), 10–13 (in French).—A method proposed by Wazek and Kratzl (*Chem. Ber.*, 1943, **76**, 1209), and based on the pptn. of the aldehyde bisulphite compounds as benzylthiuronium salts, was examined. The melting-points of the benzylthiuronium derivatives of the corresponding six aldehydes studied (acetaldehyde, *iso*butyraldehyde, heptaldehyde, benzaldehyde, *o*-tolualdehyde and furfuraldehyde) are in a relatively narrow range (110° to 120°). The pyridyl aldehydes are not pptd. since a zwitter-ion of type $\overset{+}{H}NC_5H_4CHOHSO_3^-$ is formed. The benzylthiuronium derivatives can be titrated with $HClO_4$ in anhyd. acetic acid provided that the dissociation constants of the corresponding sodium bisulphite addition compounds are $>10^{-4}$. The method is therefore too limited in applicability to be recommended. E. SJÖSTRÖM

1359. **Contributions to the analytical chemistry of the aldehydes. I. Direct iodimetric determination of formaldehyde and acetaldehyde by α-hydroxysulphonates (aldehyde bisulphites).** E. Schulek and L. Maros (L. Eötvös Univ., Budapest, Hungary). *Acta Chim. Acad. Sci. Hung.*, 1958, **17** (3), 369–375 (in German).—Aldehydes are first converted into bisulphites with H_2SO_3, the excess of which is removed by titration with iodine; the soln. is made alkaline and KCN is added. The SO_3^{2-} formed are titrated with iodine after acidifying. The interference by atmospheric O is eliminated by the use of a layer of pentane on the surface of the soln., which also serves to inhibit the evolution of SO_2. The accuracy is within $\pm 0{\cdot}2\%$. Good agreement is reached with results obtained by other methods.
G. P. COOK

1360. **Identification of paraldehyde and acetaldehyde in the presence of each other by a guaiacol reaction.** E. Hjelt and A.-L. Mukula (Inst. of Forensic Med., Univ., Helsinki, Finland). *Suomen Kem., B*, 1958, **31** (1), 138–139.—A mixture containing acetaldehyde (**I**) and paraldehyde (**II**) was treated with alkaline $KMnO_4$ to oxidise **I**. Depolymerisation of **II** is then brought about by adding H_2SO_4. **I** is identified by adding guaiacol to the aldehyde - H_2SO_4 soln. According to the actual aldehyde content the soln. becomes yellow or red and, in the presence of large amounts of aldehyde, a voluminous red ppt. is formed. *Procedure*—Transfer a sample (1 ml) into each of two glass-stoppered tubes. To one add $KMnO_4$ soln. (1% in 2 *N* KOH) (0·5 ml) and heat gently on a water bath. Allow to stand for 30 min., then add saturated oxalic acid soln. (0·5 ml). Dilute the contents of the other tube with water (1 ml). To 0·5 ml of each soln. add conc. H_2SO_4 (5 ml) and cool. Add saturated aq. guaiacol soln. (3 drops), stopper the tubes, shake, and set aside for 10 min. Finally, add water (2 ml) to both tubes. If colour develops in only the

unoxidised soln., the original sample contains only **I**. If both soln. have the same colour intensity, only **II** is present. If the colour of the unoxidised sample is deeper, the original sample contains both **I** and **II**. The concn. of **I** can be estimated from the intensity of the colour. In the oxidised sample, methanol, ethanol and formaldehyde, and, in the unoxidised sample, aliphatic alcohols from methanol to pentanol and the corresponding carboxylic acids do not interfere in concn. < 10 mg per ml. Details are given for eliminating interference from formaldehyde and alcohols present in higher concn.

E. SJÖSTRÖM

1361. **Determination of chloral hydrate, trichloroacetic acid and trichloroethanol.** P. J. Friedman and J. R. Cooper (Dept. of Pharmacol., Yale Univ. School of Medicine, New Haven, Conn., U.S.A.). *Anal. Chem.*, 1958, **30** (10), 1674–1676.—Mix pyridine (5 ml) with 1 ml of a soln. containing chloral hydrate (**I**), or trichloroacetic acid (**II**) (0·02 to 0·2 μmole) and trichloroethanol (**III**) (0·1 to 0·8 μmole). Add 36% w/w aq. KOH soln. (2 ml), mix again and place in a bath of boiling water for exactly 4 min. Cool in ice for 3 to 5 min., add a 3-ml aliquot of the pyridine layer to H_2O (0·5 ml) and measure immediately at 370 mμ and 440 mμ. **I**, **II** and **III** absorb light at 370 mμ; only **III** absorbs at 440 mμ. To determine **II** alone, mix another 1 ml of soln. with 36% KOH soln. (2 ml), heat in a bath of boiling water for 2 min., cool in ice for 2 or 3 min., mix with pyridine (5 ml), place in a bath of boiling water for 4 min., cool in ice, add a 3-ml aliquot of the pyridine layer to H_2O (0·5 ml) and measure at 370 mμ. **I** is determined by difference with an error of $\simeq \pm 5\%$; for **II** and **III** the error is $\simeq \pm 3\%$.

A. R. ROGERS

1362. **Determination of the equivalent weights of organic acids by their S-benzylthiuronium derivatives.** R. Setton (Lab. de Prof. Hackspill, Chim. Min. A, Fac. des Sci., 1 Rue Victor-Cousin, Paris, France). *Bull. Soc. Chim. France*, 1958, (6), 861–863.—A weighed amount of the pptd. S-benzylthiuronium salt of an organic acid is dissolved in ethanol and treated with a standard solution of KOH - K_2HgI_4 - KI prepared by dissolving 2·1661 g of HgO and 9·9612 g of KI in 200 ml of water. The KOH used up is determined acidimetrically (bromothymol blue or potentiometrically), or the conversion of HgI_4^{2-} into $4I^-$ can be followed argentimetrically by using a silver electrode after adjustment of the pH to 3. The argentimetric method is more useful with a polybasic acid as, for example, phosphoric acid.

E. J. H. BIRCH

1363. **Determination of β-chloropropionic acid in mixtures with propionic and α-chloropropionic acids. Isotope dilution method.** J. G. Burtle, J. P. Ryan and Sr. Marie James (Gibbons) (Minnesota Mining and Mfg Co., St. Paul, Minn., U.S.A.). *Anal. Chem.*, 1958, **30** (10), 1640–1643.—Mix the sample (50 g) with ^{14}C-labelled β-chloropropionic acid, add CuCl (0·5 g) to inhibit polymerisation of any acrylic acid present and remove propionic and α-chloropropionic acids by distillation under reduced pressure. Purify the solid residue by fractional vacuum-sublimation, melt the isolated β-chloropropionic acid ($\simeq 0{\cdot}5$ g), deposit on a special planchet and count as an "infinitely thick" layer of supercooled liquid. The background count is large and variable and must be measured immediately before and after each sample count.

A. R. ROGERS

1364. **Infra-red spectra of carboxylic acid hydrazides.** D. Prevoršek (Lab. de Rech. Phys., 1 rue Victor-Cousin, Paris, France). *Bull. Soc. Chim. France*, 1958, (6), 795–801.—The infra-red spectra of normal and deuterated hydrazides of various carboxylic acids are studied in solution in $CHCl_3$ and in the solid state. Bands at 3450 cm^{-1} and at 3330 cm^{-1} are attributed, respectively, to ν (bond-stretching) (N–H) and ν (N–H) (asymmetrical) the latter being slightly lowered in wave number owing to hydrogen bonding with the carbonyl group. This is confirmed by the increase in intensity of the band in more concentrated solution. In the solid state both bands are lowered in wave number by intermolecular hydrogen bonding. In the solid state a single large band at 1670 to 1620 cm^{-1} is found for aliphatics and two peaks of different intensity in the same region for aromatics. In solution the peaks diverge and are attributed to ν(C=O) and δ (angle-deformation) ($N–H_2$). There are two strong maxima between 1570 and 1380 cm^{-1}, being displaced towards 1470 and 1300 cm^{-1} in solution. There is considerable displacement by isotopic substitution and this is explained by a coupling between δ(N–H) and ν(C–N) which is not possible after deuteration. The band ν(C=O) is also effected by deuteration, implying a coupling between ν(asymmetrical) $\begin{matrix} O \\ \diagdown \\ C \\ \diagup \\ N \end{matrix}$ and δ(N–H). The effects are compared with those in secondary amides.

E. J. H. BIRCH

1365. **Quantitative determination of a series of malonic esters by gas chromatography.** J. B. Tepe and H. J. Wesselman (Eli Lilly and Co., Indianapolis, Ind.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1958, **47** (6), 457–458.—A mixture containing diethyl malonate and its ethyl, diethyl, *iso*amyl, *iso*amylethyl and di*iso*amyl homologues can be qual. and quant. analysed by gas chromatography with a column of 20% w/w Linde Silicone Oil L-46 on Celite C-44857 at 220° and with He as carrier gas.

A. R. ROGERS

1366. **Colorimetric determination of hexamine.** D. Beranová and S. Hudeček (Res. Inst. Synth. Resins, Pardubice, Czechoslovakia). *Chem. Průmysl*, 1958, **8** (4), 218–220.—The method is based on the determination of formaldehyde liberated by hydrolysis of hexamine and water-sol. nitrogen-containing compounds, and is suitable for application to phenolic moulding compounds and mouldings. *Procedure*—Extract the sample (0·15 g) in water (500 ml), and to a 50-ml aliquot of the soln. add H_2SO_4 (50%) (10 ml) and distil off a portion. To 1 ml of the distillate add 5 ml of buffer soln. (pH 3) (citric acid - Na_2HPO_4) and 5 ml of the reagent (dissolve 0·5 g of methyl violet 2B in 400 ml of hot H_2O, cool, and add 5 ml of conc. HCl and 12·1 g of cryst. Na_2SO_3; dissolve, add 5 ml of conc. HCl, dilute with H_2O to 500 ml, set aside for 12 hr. and filter through activated charcoal). After 1 hr. measure the extinction with a green filter BG 7. The error is ±2%.

J. ZÝKA

1367. **Potassium persulphate as a volumetric reagent. Determination of organic derivatives of hydrazine.** Balwant Singh, S. S. Sahota and Iqbal Singh (Panjab Univ., Hoshiarpur, India), *Z. anal. Chem.*, 1958, **162** (4), 256–259 (in English).—Potassium persulphate soln. (0·04 *M*) is used as a volumetric reagent for the quant. determination of

a series of organic hydrazine derivatives in conc. HCl soln. at room temp. The catalyst and peroxidiser is ICl. To the pure substance (7 to 56 mg) were added approximately 10 ml of H_2O and HCl to a concn. of 6 to 7·5 *N*, followed by 5 ml of 0·02 *M* ICl and 5 ml of $CHCl_3$. The cold mixture was titrated with 0·04 *M* $K_2S_2O_8$ to a pale-yellow end-point due to free ICl. Duplicate results from 11 hydrazine derivatives are tabulated. S. BAAR

1368. **Polarographic determination of alkyl nitrites.** I. V. Patsevich, A. V. Topchiev and V. Ya. Shtern (Inst. of Petroleum, Acad. Sci., USSR, Moscow). *Zhur. Anal. Khim.*, 1958, **13** (5), 608–612.—Alkyl nitrites may be determined polarographically in alkaline media. For ethyl and butyl nitrites in an alkaline (LiOH) medium the $E_{\frac{1}{2}}$ is −0·65 V. For ethyl nitrite it is shown that the wave height is proportional to the concn., that the $E_{\frac{1}{2}}$ is practically independent of pH in the range 8·6 to 12·3, and that increasing the temp. of the soln. by 1° decreases the wave height by 1·4 to 1·6%. At pH 12·3 the wave height for ethyl nitrite is practically constant for 1 hr., decreasing to one-half of its value in 24 hr. C. D. KOPKIN

1369. **Near-infra-red data on oximes at 2·78 microns.** R. F. Goddu (Hercules Powder Co., Inc., Res. Centre, Wilmington, 99, Del., U.S.A.). *Anal. Chem.*, 1958, **30** (10), 1707–1708.—Oximes have an extremely intense fundamental hydroxyl band at 2·78 μ with molar absorptions 3 to 4 times that of most alcohols and hydroperoxides, so that it should be possible to determine very small amounts of oximes. Alcohols and hydroperoxides should not interfere, but phenols will, and it should be possible to determine oximes in the presence of most other nitrogen-containing compounds. As dilution considerably affects the absorptivities of ketonic oximes it will be desirable to work from a calibration curve in this case. K. A. PROCTOR

1370. **Evaluation of six methods for determination of nitrogen in nitroguanidine.** M. I. Fauth and H. Stalcup (U.S. Naval Powder Factory, Indian Head, Md., U.S.A.). *Anal. Chem.*, 1958, **30** (10), 1670–1672.—The method of Bowman and Scott is imprecise and is not recommended. The nitrometer method gives slightly high results of good precision, although the $TiCl_3$ and trans-nitration methods are probably equally satisfactory for the assay of nitro-group N. For the assay of total N, the Dumas method is preferred to that of Kjeldahl. A. R. ROGERS

1371. **Esters containing phosphorus. XVI. A new colour reaction for the detection and estimation of dialkyl phosphites.** B. C. Saunders and B. P. Stark (Univ. Chem. Lab., Cambridge). *Tetrahedron*, 1958, **4** (1–2), 197–198.—A blue or purple colour is obtained on treatment of an alkaline soln. of *m*-dinitrobenzene with several dialkyl phosphites. A wide variety of substituted *m*-dinitrobenzenes may be used, but the reagent of choice is 3:5-dinitrobenzoic acid which is soluble in aq. media and produces an intense colour. Fairly stable colours are obtained if the reaction is carried out in a saturated soln. of $NaHCO_3$. The test is sensitive to a phosphite concn. of 1 in 1×10^4.

XVII. Detection and estimation of dialkyl phosphites in the presence of trialkyl phosphites. B. C. Saunders and B. P. Stark. *Ibid.*, 1958, **4** (1–2), 198–200.—A rough estimation of the amount of trialkyl phosphite is obtained by titration against iodine with which dialkyl esters do not react appreciably. Addition of alkaline 3:5-dinitrobenzoate to the mixture thus obtained permits colorimetric determination of the dialkyl phosphite. K. R. C.

1372. **Absorption spectra of benzene derivatives in the region 5 to 6 μ.** E. A. Glebovskaya, A. A. Zakharov, I. K. Lapina and Z. G. Kaplan. *Trudy Vses. Neft. Nauch.-Issled. Geologorazved. Inst.*, 1957, (105), 23–36; *Ref. Zhur., Khim.*, 1958, (20), Abstr. No. 67,343.—The i.r. spectra of 12 mono-substituted benzene hydrocarbons, aniline, dimethylaniline, 14 disubstituted benzene hydrocarbons, 2 tetrachlorobenzenes, certain tri-, tetra- and penta-substituted benzene hydrocarbons, and mono-, di- and tri-substituted naphthalenes at 5 to 6 μ are measured and studied; the absorption curves are given. C. D. KOPKIN

1373. **Analysis of the composition of mixtures of the isomers of xylene by viscosity and freezing-point.** V. M. Olevskiĭ and I. F. Golubev. *Trudy Gos. Nauch.-Issled. i Proekt. Inst. Azotn. Prom.*, 1957 (7), 316–322; *Ref. Zhur., Khim.*, 1958, (20), Abstr. No. 67,344.—To determine the content of the isomers of xylene in ternary mixtures not containing impurities, first determine the content of *o*-xylene (**I**) by measurement of the viscosity at 100°; at this temp. the viscosities of the *m*- and *p*-isomers coincide. The concn. of the *m*- (**II**) and *p*- (**III**) isomers may be found by three methods—(*i*) determine the content of **II** by boiling the mixture with dil. HNO_3 by Konovalov's method, and, knowing the amount of **I**, calculate the content of **II**; (*ii*) measure the viscosity of the ternary mixture at 0°, at which temp. the viscosity depends on the content of **II** and **III**. Knowing the content of **I** and using the viscosity curve of the isomers, determine the content of **II** and **III**. The method is suitable for a content of **I** of 30% to 80%. (*iii*) Measure the f.p. of the ternary mixture; using the known dependence of the f.p. on the content of **III**, the **III** may be determined, and, knowing the content of **I**, the amount of **II** may be calculated. The accuracy of the analysis is 2%. C. D. KOPKIN

1374. **Gas-chromatographic separation of *meta*- and *para*-xylenes in aromatic mixtures.** A. Zlatkis, L. O'Brien and P. R. Scholly (Univ. of Houston, Texas, U.S.A.). *Nature*, 1958, **181**, 1794.—The xylene isomers have been resolved by gas-liquid chromatography in a mixture with benzene, toluene and ethylbenzene under the following conditions—column dimensions, 5 metres × 5 mm; column temp., 100°; stationary phase, 15% (w/w) benzyldiphenyl on "Chromosorb" 60 to 80 mesh; carrier gas, He at 59 lb per sq. in. inlet pressure and a flow rate of 100 ml per min.; sample charge, 0·005 ml; number of theoretical plates, 9500; time, 93 min. G. BURGER

1375. **Comparison of methods for the colorimetric determination of phenols.** Satoyoshi Osaki (Kamaishi Works, Fuji Iron and Steel Co., Kamaishi, Iwate-ken). *Japan Analyst*, 1958, **7** (5), 275–283.—The determination of a small amount (<10 p.p.m.) of phenol, *o*-, *p*- and *m*-cresol and tar acid in waste water was examined by the *p*-nitroaniline, the 4-aminophenazone and the nitrosation methods. The first two methods are applicable to the determination of the sum of the phenols when the extinction is measured at 517 mμ. The optimum wavelength for the last method is 420 mμ. The

second method appears to be the most sensitive; for <2 p.p.m. of phenols, 2% 4-aminophenazone soln. (0·3 ml) and 2% $K_3Fe(CN)_6$ soln. (1 ml) suffice, whereas for <50 p.p.m. of phenols, 10% soln. of both reagents (1·5 ml and 4·0 ml, respectively) are preferred. Since the sensitivity of these phenols to the nitrosation method is similar, this method is the most suitable for the determination of their sum. When other methods are used, the working curve should be prepared with a standard soln. of a similar composition.

K. SAITO

1376. **Paper chromatography of 2:4-dinitrophenylhydrazones of aromatic carbonyl compounds.** E. Sundt and M. Winter (Res. Lab., Firmenich & Cie, Geneva, Switzerland). *Anal. Chem.*, 1958, **30** (10), 1620–1622.—The 2:4-dinitrophenylhydrazones of aromatic aldehydes and ketones may be separated by descending chromatography on strips of Whatman No. 7 paper, cut across the fibres, with dimethylformamide as stationary phase and *cyclo*hexane - *cyclo*hexene (5:3) as mobile phase. Thorough equilibration of the atmosphere is especially important. To increase the sensitivity, and to aid identification of the pale-yellow spots, the developed chromatogram is sprayed with 10% NaOH soln. and examined by visible and u.v. light.

A. R. ROGERS

1377. **Determination of *cyclo*hexanone in the presence of other ketones.** A. S. Maslennikov (Prophylactic Disinfection Lab., Gorki Sanitary-Epidemic Station). *Zhur. Prikl. Khim.*, 1958, **31** (8), 1277–1280.—An absorptiometric method and a colorimetric titration method based on the reaction of *cyclo*hexanone with diazonium salts of H-acid are described. The former is applicable in the presence of fivefold amounts and the latter in the presence of 30-fold amounts of other ketones. The aq. soln. (1 ml) containing *cyclo*hexanone and other ketones is mixed with 0·2-ml amounts of a 0·25% soln. of the monosodium salt of H-acid in 0·1 *N* H_2SO_4, 1% $NaNO_2$ soln., 5% sodium metabisulphite soln. and 10% NaOH soln., and diluted to 10 ml after 5 min. The colour is compared with that of standards. For colorimetric titration the sample (2 ml), containing >1 mg of ketones in all, is mixed with 1 ml of a 1% soln. of H-acid in 0·2% H_2SO_4 and shaken with 0·2 ml of 5% $NaNO_2$ soln. Then 1 ml of a 1:1 mixture of 20% soln. of Na_2SO_3 and NaOH is added. A cherry-red colour appears in the presence of *cyclo*hexanone. After 10 min., 0·5 ml of 50% H_2SO_4 soln. is added. The azo dye formed by reaction with *cyclo*hexanone is pptd. Products of the reactions with other ketones remain in soln. The ppt. is filtered off and washed twice with ethanol, and then dissolved in 10 ml of water. A standard aq. soln. of the azo dye is added to water until the colour matches that of the sample soln.

G. S. SMITH

1378. **Determination of *cyclo*hexanone and *cyclo*hexanol when present together.** A. S. Maslennikov (Gorki Regional Sanitary-Epidemic Station). *Zhur. Anal. Khim.*, 1958, **13** (5), 599–602.—The determination of *cyclo*hexanone is based on the formation of a cherry-red azo dye with a diazonium salt derived from H-acid (**I**), one molecule of *cyclo*hexanone reacting with two molecules of the diazo salt. The resulting soln. obeys Beer's law and has max. absorption at 550 mμ. The sensitivity is 0·2 μg per ml. The mol. extinction coeff. is 15,700. To 1 ml of the soln. to be analysed add 0·2 ml of a 10% soln. of hexamine and 0·02 ml of acetic anhydride (to prevent oxidation of *cyclo*hexanol to *cyclo*hexanone), mix, add 0·2 ml of a freshly prepared 1% soln. of sodium metabisulphite, 0·2 ml of 25% NaOH soln. and 0·5 ml of a freshly prepared soln. of the diazo salt of **I**. After 5 min. make the vol. up to 10 ml and measure the extinction. Construct a calibration curve from a standard soln. of *cyclo*hexanone containing 40 μg per ml. A green filter is used for the measurements. The error of the determination is >9% for 1 to 40 μg of *cyclo*hexanone per ml in the presence of 100 times this amount of *cyclo*hexanol. The determination of *cyclo*hexanol is based on the red colour formed on heating it with diphenylamine (**II**) in H_2SO_4. Beer's law is not obeyed. The max. absorption is at 530 mμ, and the sensitivity is 5 μg per ml. To 2 ml of soln. add 2 ml of a 2% soln. of **II** in conc. H_2SO_4. Prepare a series of standards containing from 10 to 100 μg of *cyclo*hexanol. If the content of *cyclo*hexanone is >0·5 mg per ml, add 0·2 ml of a 25% aq. soln. of hydroxylamine sulphate. Place the tubes in an oil bath at 145° to 150° for 15 min. and measure the extinction. The error in determining 10 to 100 μg of *cyclo*hexanol in the presence of 30 times its quantity of *cyclo*hexanone is >12%. The method may be adapted for the determination of these compounds in air.

C. D. KOPKIN

1379. **Near-infra-red spectra of primary aromatic amines.** K. B. Whetsel, W. E. Roberson and M. W. Krell (Tennessee Eastman Co., Kingsport, Tenn., U.S.A.). *Anal. Chem.*, 1958, **30** (10), 1598–1604.—Data are given for aniline and 39 of its substituted derivatives, with particular reference to the N–H bands between 1·0 and 2·0 μ. The positions and intensities of the bands can be correlated with the electronic nature and position of the substituents.

K. A. PROCTOR

1380. **Near-infra-red analysis of mixtures of primary and secondary aromatic amines.** K. Whetsel, W. E. Roberson and M. W. Krell (Tennessee Eastman Co., Kingsport, Tenn., U.S.A.). *Anal. Chem.*, 1958, **30** (10), 1594–1597.—By using the N–H overtone and combination bands near 1·49 and 1·97 μ, respectively, mixtures of aniline and N-ethylaniline containing up to 99% of either constituent can be analysed with a standard deviation of about ±1%. By modifying the method, aniline in the range 0 to 10% can be determined with a standard deviation of ±0·1%. Aliphatic amines and tertiary aromatic amines do not interfere.

K. A. PROCTOR

1381. **Determination of methyl mercaptan or of methanol in methyl mercaptan in their dilute aqueous solutions.** A. von Wacek and J. Smitt-Amundsen (Tech. Hochschule, Graz, Austria). *Monatsh. Chem.*, 1958, **80**, 110–115.—The previously described method and apparatus (*cf.* Wacek and Zeisler, *Anal. Abstr.*, 1955, **2**, 1826) were tested for the analysis of known mixtures of methyl mercaptan and methanol. The soln. of known methyl mercaptan content were prepared by saponification of methyl *p*-nitrothiolobenzoate and the methanol by saponification of methyl *p*-nitrobenzoate. In the presence of 0 to 7·7 mg of methyl mercaptan, 0·1 mg of methanol was detected with results 98·5 to 100·5% of those expected. The method was used for the determination of the methanol content of two different samples of black liquor.

CHEM. ABSTR.

1382. **Determination of combining weight of sulphonates.** C. M. Gardner, C. H. Hale, E. A. Setzkorn and W. C. Woelfel (Development and Research Dept., Continental Oil Co., Ponca City, Okla., U.S.A.). *Anal. Chem.*, 1958, **30** (10), 1712–1713.—The method is based on the proposed ASTM procedure for the determination of S in petroleum products by rapid combustion and iodimetric titration of the SO_2 produced. The sample of sulphonate must first be purified. A barium or calcium sulphonate is first converted into the sodium salt by the method of Brooks *et al.* (*Ind. Eng. Chem., Anal. Ed.*, 1946, **18**, 544). Impurities in a sodium sulphonate are removed by the ASTM method.

A. R. ROGERS

1383. **Absorption in the infra-red of some organic derivatives of tin. Attempts at quantitative determinations.** L. Domange and J. Guy (Lab. Nat. de Contrôle des Medicaments, Fac. de Pharm., Paris, France). *Ann. Pharm. Franç.*, 1958, **16** (3), 161–169.—The i.r. spectra of pure triethyliodotin (liquid) and diethyldi-iodotin (solid) are mapped with a Baird double-beam spectrophotometer, with an absorbing medium $\simeq$0·01 mm thick. In the region of 10 μ there is a double peak for the di-iodo and a single for the iodo compound, but this (after investigation with mixtures) is attributed merely to the solid state of the di-iodo compound. Comparison of the spectra of these compounds in CS_2 at different concn. enables a plot of the log. of the concn. against transmission (%) to be made at definite wavelengths. At 8·12 and 9·80 μ, the curve for the di-iodo lies above and approx. parallel to that for the iodo compound, and at 8·48 μ the order is reversed. The transmission of a mixture of the two lies between the curves and is distinguishable at 10% of the iodo compound, more particularly at 8·12 μ. A more sensitive distinction is obtained by plotting the differences between the transmissions at 8·12 and 8·48 μ against the log. of the concn. Various samples of diethyldi-iodotin suspected of containing 7 to 8% of the iodo compound gave curves superimposable on that of the pure di-iodo compound, but it is possible that this might have been due to the presence of ethyltri-iodotin. The spectrum of triethyltin hydroxide in CS_2 is also given.

E. J. H. BIRCH

1384. **Analysis of organotin compounds.** J. W. Price (Tin Res. Inst., London). *Paint Manuf.*, 1958, **28**, 147–150.—The determination of total Sn in organotin compounds may be readily carried out by wet ashing, followed by conventional methods for inorganic Sn. Particular problems arising when only small amounts of organotin compounds are present in other materials, *e.g.*, in poly(vinyl chloride), are discussed. In biological work, tin compounds may be analysed by radiochemical methods with ^{113}Sn. Certain dialkyl- and trialkyltin compounds may be determined colorimetrically by reaction with dithizone or Na dimethyldithiocarbamate under appropriate conditions. A quant. determination of a mixture of dibutyl- and tributyltin compounds, within certain concentrations, may be made by direct or derivative polarography using the second wave of the dibutyl and the single wave of the tributyl compounds.

L. A. O'NEILL

1385. **Determination of silicon, germanium and tin in their volatile organo compounds.** M. P. Brown and G. W. A. Fowles (Chem. Dept., Southampton Univ., England). *Anal. Chem.*, 1958, **30** (10), 1689–1691.—Bubble O through the weighed sample until evaporation is complete ($\simeq$90 min.) and for a further 15 min. Pass the vapours into a weighed silica tube and ignite in a plug of prepared asbestos. Remove the tube, ignite it to constant wt. at 800° and calculate the wt. of oxide obtained. With highly volatile samples or with samples of high b.p., control the temp. during evaporation by use of a cold bath or an i.r. lamp. A slightly modified procedure is given for the analysis of samples that hydrolyse readily to non-volatile products. The results are accurate to $\pm$0·5% for all 13 substances tested. An analysis is normally completed in 3 to 4 hr.

A. R. ROGERS

1386. **Paper chromatography and paper electrophoresis of organic compounds. I. Behaviour of 1-phenylazo-2-naphtholsulphonic acids in salting-out-type paper chromatography.** Heijiro Ojima (Chem. Dept., Aichi Gakugei Univ., Okazaki). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1958, **79** (3), 261–263.—The relationship between the R_F value and the structure in the naphthol AS series was investigated on the basis of the difference in R_F value at various pH values and by the use of a developer at various concn. (0·001 to 1 *M* KCl containing 0·03 *N* KOH or HCl to adjust the pH). G- and R-acid derivatives having two $-SO_3H$ groups exhibit greater sensitivity towards change in concn. of KCl than do C-, F- and S-acid derivatives. On addition of ethanol to the developer, the first two groups of derivatives show max. R_F values at 50% (v/v) concn., whilst the last three show monotonically increasing R_F.

K. SAITO

1387. **Paper-chromatographic evaluation of the purity of some commercially important anthraquinone derivatives.** M. Matrka and F. Navrátil (Res. Inst. Org. Synth., Pardubice-Rybitví, Czechoslovakia). *Chem. Prûmysl*, 1958, **8** (4), 188–190.—The paper was impregnated with a 10% ethanolic soln. of 1-bromonaphthalene. The samples (5 to 20 μg) were dissolved in pyridine and developed by use of the ascending technique with 80% acetic acid. The R_F values of the separated derivatives were determined. Twelve combinations of anthraquinone derivatives were separated with this procedure. In some cases the zone-chromatographic method of separation was suitable. The separated coloured compounds were detected visually; for anthraquinonesulphonic acids, chloroanthraquinone and leucoquinizarin, u.v. light was necessary for the detection.

J. ZÝKA

1388. **The analysis of a mixture of pyridine bases by means of paper chromatography.** J. Brandsch. *Rev. Chim., Bucharest*, 1958, **9** (6), 334–335.—A method is described for the separation of α- and γ-picolines and two other constituents from a mixture of bases obtained from the condensation of NH_3 and acetaldehyde. Strips of paper (3 cm × 45 to 50 cm) are suspended in a chamber, with the top ends dipping in a flask of 0·2 *N* HCl. After being washed, the paper is dried and saturated with formic acid. A 1-cm spot of the sample (2% soln. in 2 *N* HCl) is applied and allowed to dry. The developer is butanol saturated with 2 *N* HCl. The descending technique is used because of the small difference in R_F between the two picolines. The spots are revealed by spraying with 0·1 *N* iodine.

H. SHER

1389. **Liquid fuels. I. Sampling. II. Testing methods and their interpretation. Progress Review No. 43.** C. W. G. Martin (Liquid Fuels and Gas

Dept., Shell Petroleum Co., Ltd., London). *J. Inst. Fuel*, 1958, **31**, 274–278.—In sampling a batch of oil which is too viscous to be made uniform by mixing, portions are drawn from specified levels (*cf.* "Inst. Petrol. Standard Methods," 17th Ed., London, 1958. IP 51/58); usually the portions are drawn equally from levels one-sixth, one-half and five-sixths of the total depth. In commercial practice, tests are mutually confirmatory if they fall within given ranges of repeatability (by one observer) or reproducibility (by different observers), or between "confidence limits" within which 95% of test results are statistically expected to fall. The choice of tests for specifications of fuel oils is discussed. Pour-point is unsuitable since it may depend on the immediately prior treatment of the oil. Specific gravity has little significance. Coal-tar fuels are classed according to the temp. (° F) at which their viscosity is low enough for efficient atomising. (*Cf.* B.S.S. 1469:1948. "Coal Tar Fuels," Assoc. of Tar Distillers.) A. R. PEARSON

1390. **Rapid polarographic method for hydroperoxides in gasolines.** M. L. Whisman and B. H. Eccleston (Bureau of Mines, U.S. Dept. of the Interior, Bartlesville, Okla., U.S.A.). *Anal. Chem.*, 1958, **30** (10), 1638–1640.—The results obtained by the method described compare well with those obtained by chemical and other polarographic procedures. An analysis can be performed in about 6 min. K. A. PROCTOR

1391. **Polarographic determination of benzene in commercial petrol.** V. Šedivec (Inst. Hyg. and Ind. Diseases, Prague). *Chem. Průmysl*, 1958, **8** (4), 180–183.—The method is based on nitration of all the hydrocarbons present, the selective oxidation of the nitration products of toluene and xylene, and the isolation of dinitrobenzene by extraction with pyridine, and its polarographic determination. *Procedure*—Measure the sample (≃0·8 g) into a 10-ml flask containing anhyd. acetic acid (5 ml) and dilute to vol. with the same solvent. Into a 50-ml flask measure the nitration mixture (10 g of dried NH_4NO_3 dissolved in 100 ml of conc. H_2SO_4) (2 ml), and add 0·5 ml of the sample soln. After 10 min. add a satd. soln. of CrO_3 (0·1 ml), mix and heat for 30 min. on a water bath (90° to 100°) (if, during this heating, the colour turns bluish green, add more CrO_3 soln.). Cool with H_2O and add methanol (20%) dropwise until the colour is bluish green, dilute with H_2O (10 ml) and add pyridine (10 ml). Cool and add NaOH soln. (40%) (15 ml), transfer to a separating funnel, wash the residue with 5 to 10 ml of water, combine the liquids and set aside. Separate the lower green layer, wash the pyridine layer with NaOH soln. (20%) (5 ml) and separate again. Transfer the pyridine layer to a 50-ml flask, wash the separating funnel with H_2O, and add to the combined liquids diluted nitration mixture (1:5) (10 ml) and gelatin soln. (2 ml). Dilute to vol. with H_2O and register the polarographic wave. Compare with a calibration curve. A method for the determination of the total content of aromatic compounds is also described. J. ZÝKA

1392. **Analysis of aromatic fractions of kerosine by phosphorescence spectra.** Kh. I. Mamedov. *Optika i Spektroskopiya*, 1957, **3** (6), 587–591; *Ref. Zhur., Khim.*, 1958, (19), Abstr. No. 64,266.—The composition of aromatic fractions of kerosine of boiling-range 225° to 300° is studied by using the spectra of the persistent radiation at the temp. of liquid N. The naphthene and paraffin hydrocarbons are separated with silica gel, and the aromatic hydrocarbons remaining are separated by distillation and chromatography and identified by their decomposition points and as picrates. The spectra of the ten fractions obtained, cooled in *iso*octane, are photographed at 77° K on a spectrograph with an exit collimator and with a single-disc phosphoroscope, with a rate of rotation of the disc of 2000 r.p.m. The spectra show clearly the bands due to the main components. In the fraction $C_{11}H_{10}$ (boiling-range 242° to 255°, n_D^{20} 1·6088, d_4^{20} 1·0071), 1-methylnaphthalene is predominant, together with a small amount of 2-methylnaphthalene (max. at 515 mμ) and dimethylnaphthalenes (**I**) (bands at 485, 523 and 563 mμ). The $C_{15}H_{18}$ fraction (boiling-range 270° to 275°, n_D^{20} 1·5815, d_4^{20} 0·9767) contains dialkylnaphthalenes (the bands due to **I** coincide with the bands due to ethylmethylnaphthalenes) and trimethylnaphthalenes (**II**) (bands at 491, 529 and 570 mμ). The $C_{13}H_{14}$ fraction (boiling-range 262° to 268°, n_D^{20} 1·6062, d_4^{20} 1·0055) and the $C_{15}H_{18}$ fraction (n_D^{20} 1·5851, d_4^{20} 0·9792) also comprise **I** and **II**, the latter predominating in the second fraction. In the $C_{12}H_{12}$ fraction (b.p. >270°, n_D^{20} 1·6060, d_4^{20} 1·0044), beside **I** and **II** there are traces of tetramethylnaphthalenes (**III**) (humps at 500 and 535 mμ). The $C_{13}H_{14}$ fraction (boiling-range 278° to 285°, n_D^{20} 1·5962, d_4^{20} 0·9955) and the $C_{13}H_{14}$ fraction (boiling-range 270° to 275°, n_D^{20} 1·6060, d_4^{20} 1·0055) contain mainly **II** with small amounts of **I** and **III**. In the $C_{13}H_{14}$ fraction (boiling-range 280° to 287°, n_D^{20} 1·6030, d_4^{20} 1·0013) there are various types of **II**. The fractions $C_{14}H_{16}$ (boiling-range 283° to 290°, n_D^{20} 1·6050, d_4^{20} 1·0099) and $C_{14}H_{16}$ (m.p. 180° to 182°) consist mainly of **III** (max. at 499 and 537 or 538 mμ). With increase of b.p. of the fractions the origin of the spectra moves towards longer wavelengths. As the number of substituents in the naphthalene nucleus increases, the spectra are displaced into the long-wave region. C. D. KOPKIN

1393. **Determination of paraffin content of crude petroleum residues.** V. Beneš (Refinery of Mineral Oils, Pardubice, Czechoslovakia). *Chem. Průmysl*, 1958, **8** (4), 191–192.—The method is based on the removal of resinous compounds on activated charcoal and the separation of solid paraffins with ethanol from ethereal soln. J. ZÝKA

1394. **Analysis of hydrocarbons. 5. Analysis and evaluation of crude petroleum. II. Experimental results.** H. Grosse-Oetringhaus (Heimfelder Str. 69, Hamburg-Harburg, Germany). *Erdöl u. Kohle*, 1958, **11** (6), 383–390.—Fractions distilled from crude oils in the apparatus described conform to standard requirements. In the vacuum stage of the distillation the onset and progress of cracking can be followed by means of the attached McLeod gauge; vacuum-distillation curves had repeatability of ±3% and reproducibility of ±5%. To obtain a residue of softening-point (ring and ball) <40° without incipient cracking, a high vacuum must be maintained in the distillation vessel in the final stage, for which purpose a short, wide (3 cm) offtake is provided. Parallel tests on seven crude oils in five laboratories gave yields of light oil, gas oil, lubricating oil, and residue differing by >0·5% from the mean values. A. R. PEARSON

1395. **Determination of the volatility of oils and greases.** F. K. Volȳnets. *Zhur. Prikl. Khim.*, 1958, **31** (6), 863–868.—A uniform layer ($\simeq 60\ \mu$ thick) of the sample (5 to 60 mg) is placed on a piece of paper or foil (20 mm × 25 mm) which is suspended by means of a thin wire to the end of a horizontal glass pointer which can be viewed by means of a measuring microscope. From the degree of bending of the pointer, the weight of the load can be determined to within 0·05 mg. The suspended paper or foil is contained in a vessel immersed in a thermostat. A stream of dry N is passed through the vessel and the loss in weight of the sample is measured periodically without interrupting the experiment. G. S. SMITH

1396. **Mass-spectrometric analysis of high-boiling coal-hydrogenation products using low-ionising voltage.** A. G. Sharkey, jun., G. Wood and R. A. Friedel (Bureau of Mines, Region V, U.S. Dept. of the Interior, Bruceton, Pa., U.S.A.). *Chem. & Ind.*, 1958, (26), 833–834.—By the use of low-energy electrons, spectra containing only molecule-ions or only molecule-ions of the aromatic and unsaturated types can be obtained. From the spectra of the urea raffinate and the corresponding urea complex of a predominately saturated fraction of coal-hydrogenation middle oil and of a phenolic fraction and its trimethylsilyl ether derivatives, the mol. wt. distribution has been determined and some specific compounds have been identified. These spectra were produced in a mass spectrometer with an inlet system heated to 250° and with an ionising voltage of 7·0 V. G. BURGER

1397. **Identification of low-boiling sulphur compounds in Agha Jari (Iran) crude oil by gas - liquid chromatography.** H. J. Coleman, C. J. Thompson, C. C. Ward and H. T. Rall (Bureau of Mines, U.S. Dept. of the Interior, Bartlesville, Okla., U.S.A.). *Anal. Chem.*, 1958, **30** (10), 1592–1594.—Eleven compounds have been identified and the identification confirmed by trapping the fractions producing the chromatographic peaks and analysing them by mass spectrometry. K. A. PROCTOR

1398. **Paper-hanging pastes and powders.** British Standards Institution (2, Park St., London). B.S.3046:1958, 11 pp.—Specifications are laid down for the preparation of powder pastes, the physical properties (spread, body, tack and slip) and chemical properties (absence of staining, chloride content and pH) of the prepared paste, deterioration on storage and, after making up, efficiency of adhesion when used with the intended paper, and marking of the package. Apparatus and methods are specified for the determination of total alkali content, keeping qualities and efficiency of adhesion. R. E. ESSERY

1399. **Revised and new standards of the Essential Oil Association of U.S.A.** Essential Oil Association of U.S.A. (2, Lexington Ave., New York 10). *Perfum. Essent. Oil Rec.*, 1958, **49** (6), 303–305.—New specifications covering oils of cumin, orris root, tansy, yara yara, laurel leaf, basil (Réunion), *Abies alba*, estragon, *Eucalyptus citriodora*, and *Pinus sylvestris*, and allyl caproate, undecylic aldehyde, benzyl cinnamate, citronellyl acetate, cedryl acetate, methyleugenol, diphenylmethane, (−)-carvone, (+)-carvone and phenylacetaldehyde dimethyl acetal are reviewed and principal requirements are quoted. The specifications "Determination No. 1, p. 5" (determinations of esters and free phenols) and "E.O.A. Apparatus 2 (vacuum-distillation apparatus)," have been issued. Revised standards for oils of lemongrass and amyris are quoted. H. B. HEATH

1400. **The analysis of rose oils by vapour-phase partition chromatography and by infra-red spectroscopy.** Y.-R. Naves (L. Givaudan & Cie, Vernier-Geneva, Switzerland). *Perfum. Essent. Oil Rec.*, 1958, **49** (6), 290–291.—The assay and evaluation of rose oils by an examination of their gas chromatograms is described. Genuine rose oils show peaks corresponding to ethanol, *n*-nonanal, 2-phenylethanol, then, together, rhodinol (citronellol) and nerol, followed by geraniol, methyleugenol and finally the stearoptenes. Oils adulterated with dihydrocitronellol show an additional peak before that of rhodinol and nerol. The relative proportions of these constituents are determined by measurement of the absorption at 1593, 1047, 858, 748 and 725 cm^{-1} for 2-phenylethanol, 1234 cm^{-1} and 1002 cm^{-1} for geraniol and nerolidol, 1096 cm^{-1} for geraniol, 1142 and 1087 cm^{-1} for nerol and 1057 cm^{-1} for rhodinol. Several chromatograms and infra-red spectra are illustrated and discussed. H. B. HEATH

1401. **Determination of essential oils in soaps and cosmetic preparations.** A. Ady and L. Hunyady (Staatl. Kontroll-Lab. für die Pflanzenöl-Ind., Budapest). *Fette, Seif., Anstrichmitt.*, 1958, **60** (5), 378–379.—The method of the authors (*Anal. Abstr.*, 1957, **4**, 2685) for the determination of essential oil in perfume is applied to perfumed soap and to liquid and powder cosmetic preparations. The determination on soaps is carried out on a light-petroleum (40°) extract; liquid cosmetic preparations and powders are extracted with diethyl ether, the latter in a Soxhlet apparatus. E. HAYES

1402. **Determination of acid retained in cellulose fibre.** O. Ant-Wuorinen and A. Visapää (State Inst. for Tech. Res., Helsinki). *Suomen Kem., B*, 1958, **31** (1), 90–95.—Samples of cotton linters, bleached sulphite pulp, and viscose rayon were allowed to stand in 0·1 *N* HCl. The samples were first sucked dry and the remaining HCl was determined from the difference in wt. of the wet and dry samples and automatic titration with 0·001 *N* NaOH. In calculating the HCl content, the carboxyl content of the cellulose sample was taken into consideration. Other samples were extracted with water in an atm. of N in order to displace the HCl from the fibre as completely as possible. The traces of HCl remaining in the fibre were determined by treating the sample with 10% $AgNO_3$ soln. followed by exposure to u.v. light to produce black spots of Ag. The intensity of the produced spots was estimated by means of a densitometer and the areas were measured by using a planimeter. The results indicate that, in spite of careful washing, traces of HCl are retained in the fibre. It is stated that these traces can produce many catalytic effects and interfere with the determination of accessible carboxyl and carbonyl groups in cellulose. E. SJÖSTRÖM

1403. **Determination of nitrogen in nitrocellulose and nitric acid. I. Alkalimetric titration of nitrogen in nitrocellulose and in mixed nitric and sulphuric acids.** Tetsuro Murakami (Kogakuin, Tsunohazu, Shinjuku-ku, Tokyo). *Japan Analyst*, 1958, **7**

(5), 304–309.—Nitric oxide produced by the action of $FeSO_4$ (20 g of heptahydrate) in 6 to 8 *N* HCl (60 ml) on the sample (0·3 to 0·6 g) in a current of argon is washed with 30% NaOH soln. and converted into HNO_2 with H_2O_2 (3%, 3 ml) in the presence of O. The HNO_2 is titrated with 0·1 *N* NaOH. The reduction with Fe^{2+} is completed within 25 min. by boiling, and no N_2O is produced, as shown by mass spectrometry. The standard deviation is $\pm 0{\cdot}02\%$ and the time taken for a determination is <40 min. K. SAITO

1404. **Rapid method for the determination of lignosulphonic acids.** V. Diaconescu. *Bul. Inst. Politeh., Iaşi*, 1957, **3** (1–2), 101–106.—Dimethyl-1-naphthylamine (**I**) gives a quant. ppt. with lignosulphonic acids in an acid medium containing $\pm 0{\cdot}057$ g of HCl per ml. *Procedure*—The soln. of lignosulphonic acid (10 ml) is treated with conc. HCl and titrated with a soln. of **I** in HCl (3 *N*) containing 0·01 g per ml. A dirty yellow flocculent ppt. is formed. Paper treated with sulphanilamide reagent [1·5 g dissolved in 50 ml of water and mixed with 50 ml of $NaNO_2$ soln. (1%)] is used as external indicator. The paper is soaked in this soln., and dried in an acid-free atmosphere. It is claimed that the max. error is $\simeq 4\%$, and that the determination takes only 3 to 5 min. H. SHER

1405. **Assay of cyanoethylated cotton.** G. E. Journeay and J. E. Blackmon (Monsanto Chem. Co., Texas City, Texas, U.S.A.). *Text. Res. J.*, 1957, **27**, 166–167.—The Kjeldahl procedure when modified to eliminate the initial H_2SO_4 digestion (Daul *et al.*, *Ibid.*, 1955, **25**, 246) is not satisfactory for the assay of cyanoethylated cotton, nor do any particular advantages accrue from its use. Values found by the standard Kjeldahl method are not reproducible by the modified technique. K. R. C.

1406. **A method of determining the sulphur content of wool.** M. V. Glynn (Textile Coll., Gordon Inst. Tech., Victoria, Australia). *Text. Res. J.*, 1958, **28** (9), 744–746.—Samples of modified wool were digested with 10-ml aliquots of the digestion soln. consisting of equal vol. of $HClO_4$ (72%) and conc. HNO_3. The indicator was 0·1 *N* potassium dichromate (5 ml) giving a green - orange end-point. Sulphur was then pptd. as $BaSO_4$ and determined gravimetrically. The results were comparable with those obtained by standard micro-analytical methods when applied to virgin wools of different qualities and to wool modified to contain the more resistant monosulphide linkage of lanthionine. K. R. C.

1407. **The polarographic estimation of sulphydryl and disulphide groups in wool.** J. P. E. Human (Wool Text. Res. Lab., C.S.I.R.O., Victoria, Australia). *Text. Res. J.*, 1958, **28** (8), 647–654.—For the determination of sulphydryl S in intact wool, the wool is allowed to react with an excess of *p*-chloromercuribenzoic acid or chlormerodrin in a buffer containing urea at pH 7 to 8·5. For the determination of total sulphydryl S and disulphide S in intact wool, sulphite as well as urea is present in a buffer at pH 8·5. In both determinations excess of Hg is measured polarographically. For total sulphydryl S and disulphide S in wool hydrolysates, amperometric titration with $HgCl_2$ may be used. The method is specially modified for 10 to 100-mg samples and 0·05 to 0·10-mg samples. K. R. C.

1408. **The action of N-ethylmaleimide on wool and its use for the estimation of sulphydryl groups.** R. W. Burley and F. W. Horden (Nat. Chem. Res. Lab., C.S.I.R., Pretoria, S.A.). *Text. Res. J.*, 1957, **27**, 615–622.—In an aq. buffer soln. of pH 3·5, N-ethylmaleimide (**I**) combines slowly with intact wool but more rapidly after the wool has been pulverised. Equilibrium is reached when an amount $\simeq 30\% >$ the SH-group concn. has reacted. There does not appear to be a reaction of **I** with other groups. There is no appreciable discrepancy with copper-deficient wool. **I** can also be used to estimate the SH groups in other wools in which these groups are easily accessible and in large amounts, but not in merino wool. K. R. C.

1409. **Quantitative determination of *cyclo*hexylamine in rayon spin-baths.** M. Matell (Mo & Domsjö AB Örnsköldsvik, Sweden). *Text. Res. J.*, 1957, **27**, 993.—Dilute 100 ml of the spin-bath soln. with H_2O (100 ml) and add an excess (50 ml) of 10 *N* NaOH. Heat to boiling and collect the distillate (25 ml) in a flask containing an excess of 0·1 *N* HCl. Back-titrate with 0·1 *N* NaOH. The amount of amine is calculated from the difference between the blank and the sample. The accuracy is sufficient for practical purposes. K. R. C.

1410. **Chemical analysis of plastics. VII.** K. Thinius, E. Schroeder and U. Waurick (Inst. Chem. Tech. Plaste, Leipzig, Germany). *Plaste u. Kautsch.*, 1957, **4**, 409–413.—For the determination of the vinyl acetate content of vinyl chloride - acetate copolymers, the material is dissolved in dioxan, saponified with Na ethoxide, or NaOH - ethanediol when the vinyl acetate content is $<40\%$, diluted with H_2O, and passed through an ion-exchange column to form the free acids. The total acidity is then determined by titration, the Cl argentimetrically and the acetate is obtained by difference. Methods of measuring the volatility of plasticisers from plastic materials using activated carbon have also been examined. L. A. O'NEILL

1411. **Determination of maleic anhydride in polyesters.** P. D. Garn and H. M. Gilroy (Bell Telephone Laboratories Inc., Murray Hill, N.J., U.S.A.). *Anal. Chem.*, 1958, **30** (10), 1663–1665.—Homogeneous alkaline hydrolysis cannot be used in the determination of maleic anhydride and derivatives in polyester resins, because maleic esters and polyesters dimerise to butene-1:2:3:4-tetracarboxylates, but a two-phase saponification is satisfactory. *Procedure*—Dissolve the sample (0·2 to 2 g) in benzene (100 ml) or, with samples of high maleic content, in $CHCl_3$ (100 ml). Add *N* KOH (200 ml) and shake for 3 hr. Acidify a 10-ml aliquot of the aq. phase with 10 *N* H_2SO_4 with methyl red as indicator, add 0·2 *N* tetramethylammonium bromide in 0·05 *N* H_2SO_4 soln. (25 ml) and dilute to 50 ml. De-gas and measure the diffusion current polarographically at $-0{\cdot}40$ and $-0{\cdot}90$ V. A. R. ROGERS

1412. **Nitrogen determination in high-molecular-weight polymers.** W. Skoda and J. Schurz (Inst. physik. Chem., Univ., Graz, Austria). *Z. anal. Chem.*, 1958, **162** (4), 259–262.—A modified catalyst for the decomposition of N-containing polymers is described. The NH_3 formed was determined by the Kjeldahl method. The polymer (0·3 to 0·4 g) was digested with 40 ml of H_2SO_4 containing $CuSO_4.5H_2O$ (1 g), HgO (0·7 g), Na_2SO_4 (9 g) and

Hg (0·5 to 0·7 g). The digestion was complete after 1 hr. and the soln. was made alkaline with 40% NaOH soln. containing $Na_2S_2O_3$ (7 g). The modified method was used to determine the N content of poly(vinyl cyanide), Vinyon N, poly-(vinylpyrrolidone) and poly(vinylcarbazole). The results were compared with those obtained by the Dumas method, which gave somewhat low figures, and with the theoretical values. S. BAAR

1413. **Analysis of polyamides.** E. Schröder (Inst. Chem. Tech. Plaste, Leipzig). *Plaste u. Kautsch.*, 1958, **5** (2), 49–51; (3), 103–107.—Examples are given of the quant. analysis of simple and of binary and ternary mixed polyamides. The methods are based essentially on acid hydrolysis, treatment with ion-exchange resins, and determination of the amine and acid components. Paper-chromatographic and spectroscopic techniques, the determination of critical acid concn. (for dissolution of the polyamides) and the determination of amine end-groups are considered. L. A. O'NEILL

1414. **Determination of the hydroxyl groups in epoxy resins.** A. Bring and F. Kadleček (Spolek pro Chem a Hutní Výrobu, Ústi n.L., Czechoslovakia). *Plaste u. Kautsch.*, 1958, **5** (2), 43–48.—For determining the hydroxyl content of epoxy resins, methods based on the following principles have been examined: acetylation with pyridinium chloride (or pyridinium perchlorate) and acetic anhydride in pyridine; acetylation with acetic anhydride and acetic acid, in the presence of Na acetate or of H_2SO_4, or in absence of catalyst; acetylation with stearoyl chloride in $CHCl_3$. All methods gave results of the right order and reasonable reproducibility, but for general convenience the last-named is preferred. L. A. O'NEILL

1415. **Improved method for determining ketones in lacquer solvents. New direct application to lacquer vehicles.** G. G. Esposito and M. H. Swann (Coating and Chemical Lab., Aberdeen Proving Ground, Md., U.S.A.). *Anal. Chem.*, 1958, **30** (10), 1643–1645.—To reduce errors in the hydroxylamine hydrochloride method below 1%, attention must be paid to the concn. of alcohol at the different stages of the determination and to the choice of indicator. By a slight modification of the method recommended, ketones may be determined directly in lacquer vehicles without prior vacuum-distillation of the solvents. *Procedure*—Allow a soln. of the lacquer solvent (containing $\simeq$0·4 g of ketone) in abs. ethanol (15 ml) to react with 36% hydroxylamine hydrochloride soln. (2·5 ml) for 1 hr. at room temp. Add ethanol (85 ml) and 0·1% ethanolic thymol blue soln. (1·5 ml) and titrate with 0·2 *N* methanolic KOH to a yellow colour, which is permanent for 30 min. Shake the soln. vigorously as the end-point is approached. Apply a correction factor of 1/0·98 for incompleteness of reaction. A. R. ROGERS

1416. **Infra-red quantitative analysis data.** *Anal. Chem.*, 1958, **30** (10), 1709.—**Analysis of 2-bromoethanol, 1:2-dibromoethane, 1:1:2:2-tetrabromoethane and 1-bromo-2-(2-bromoethoxy)ethane mixtures,** L. R. Kiley. **Analysis of 2:4-dichlorophenoxyacetic acid,** L. R. Kiley.

See also Abstracts—**1178**, Detection of organic compounds with flavylium perchlorate. **1263**, Reaction of nitrates and nitramines with phosphoric acid. **1267**, Determination of As in coal ash. **1289**, Reaction of tunstates with sugars. **1315**, Determination of tropolone. **1424**, Micro-Kjeldahl method. **1596**, Applications of chronopotentiometry to organic oxidations.

4.—BIOCHEMISTRY
INCLUDING DRUGS, FOOD, SANITATION, AGRICULTURE

Biological fluids, animal and vegetable tissues

1417. **New technique for simultaneous estimation of total body water and total exchangeable body sodium using radioactive tracers.** J. A. D. Cooper, N. S. Radin and C. Borden (Veterans Admin. Res. Hosp., Northwestern Univ. Med. Sch., Chicago, Ill., U.S.A.). *J. Lab. Clin. Med.*, 1958, **52** (1), 129–137.—The method is based on the injection of a soln. containing HTO and ^{22}NaCl. After 24 hr. HTO is determined on a blood sample by a scintillation-counter technique after purification by sublimation, and ^{22}Na with a well-type scintillation counter and pulse-height-selector combination. Total Na is also determined by flame photometry. After correction for loss during the 24 hr. in urine, which is assayed by similar methods, results are calculated by the methods given. Results for normal subjects are reported and discussed. W. H. C. SHAW

1418. **Neutron activation analysis in the determination of bone sodium.** R. Druyan, T. G. Mitchell and E. R. King (U.S. Naval Hosp., Bethesda, Md., U.S.A.). *J. Lab. Clin. Med.*, 1958, **52** (2), 304–308.—In the method described, the bone sample, either intact or after ashing, is activated for 10 min. in a nuclear reactor at a flux of about 10^{12} neutrons per sq. cm per sec. Standards of NaCl are activated similarly. The activity of the ^{24}Na produced is counted after a minimum period of 3 hr. from the time of activation; after this period the ^{49}Ca also formed has decayed completely. No interference is encountered from ^{42}K, ^{38}Cl or ^{32}P. Results obtained on bone samples are discussed. W. H. C. SHAW

1419. **Chemical determination of trace elements in biological materials. XIV. Co-precipitation of silver by the use of tellurium as collector.** Kiyoshi Kudo (Chem. Dept., Fac. of Sci., Tohuku Univ., Katabiracho, Sendai). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1958, **79** (6), 689–693.—Sandell's co-pptn. of Ag with Te (*cf. Anal. Chem.*, 1951, **23**, 1863) was examined with radioactive ^{110}Ag. Less than 10 μg of Ag is almost quant. co-pptd. in 2 *N* HCl with Na_2TeO_3 (1 mg of Te per ml of 2 *N* HCl) (1 ml) and $SnCl_2$ (1·5 g in 5 ml of 2 *N* HCl) (5 ml). On the other hand, no co-pptn. of Ag occurs with the use of hydrazine as reductant. The recovery of Ag is incomplete for $<$ 1 μg (*e.g.*, 89% for 1 μg of Ag, 84% for 0·2 μg) under the given conditions.

XV. Determination of silver in peppermint leaves. Kiyoshi Kudo. *Ibid.*, 1958, **79** (6), 693–696.—Leaf ash ($\simeq$1 g) obtained at 550° to 600° is dissolved in 6 *N* HCl (3 ml), heated to dryness, mixed with 2 *N* HCl and filtered. The residue is ignited, then treated with $NH_4F.HF$ and HCl, dissolved in 6 *N* HCl and combined with the filtrate. The HCl soln. is evaporated to dryness, dissolved in 2 *N* HCl and the Ag is pptd. as described in Part XIV. The ppt. is dissolved in HNO_3 and determined colorimetrically with *p*-dimethylaminobenzylidenerhodanine (0·03% in ethanol) by Sandell's method (*loc. cit.*). K. SAITO

1420. **Determination of calcium in biological material by the chloranilate method.** N. Chiamori and R. J. Henry (Bio-Science Res. Foundation, Los Angeles, Calif.). *Proc. Soc. Exp. Biol. Med.*, 1958, **97** (4), 817–819.—The Ferro and Ham chloranilate procedure for the determination of serum calcium (*cf. Anal. Abstr.*, 1959, **6**, 1001) is investigated. Results have been compared with those obtained by the method of Clark and Collip (*J. Biol. Chem.*, 1925, **63**, 461) and found to be favourable. Modifications of the Ferro and Ham procedure are described for the determination of urinary and faecal calcium, together with an ultra-micro modification for the determination of serum calcium.
B. P. Block

1421. **Titrimetric analysis of calcium and magnesium in muscle.** D. L. Gilbert and J. McCann (Dept. of Physiol., Albany Med. Coll., Union Univ., New York). *Proc. Soc. Exp. Biol. Med.*, 1958, **97** (4), 791–793.—Relatively simple EDTA methods are described. Dissolve muscle ash in *N* HCl, precipitate Ca with ammonium oxalate and destroy the oxalate by heating with $HClO_4$. Titrate Ca with EDTA, with calcein or Cal-red as indicator. Precipitate Mg with oxine and destroy the oxine by heating with $HClO_4$. Add sufficient EDTA in the presence of calcein until the colour of the indicator changes, after which titrate the Mg with additional EDTA, with Eriochrome black T as indicator.
B. P. Block

1422. **Trace elements in human tissue. III. [Modified method for determination of] strontium and barium in non-skeletal tissues.** E. M. Sowden (Med. Res. Council Radiobiol. Res. Unit, A.E.R.E., Harwell, England). *Biochem. J.*, 1958, **70** (4), 712–715.—Determinations of Sr and Ba are made by the neutron activation method described by Sowden and Stitch for ashed bone (*Anal. Abstr.*, 1958, **5**, 601). Because of the more varied mineral composition of skeletal tissue, a more elaborate separation is needed to obtain radiochemically pure fractions of Sr and Ba. In order to obtain sufficient activity in the Sr and Ba for radio-assay, larger amounts of tissue ash are required. These are subjected to preliminary concentration of Ba and Sr so as to avoid the high radioactivity induced in gram amounts of ash after neutron activation.
J. N. Ashley

1423. **New method for determination of zinc by the use of a zinc - porphyrin complex.** G. Müller and J. Brugsch (Univ. Med. Clinic, Berlin). *Biochem. Z.*, 1958, **330** (1), 85–88.—The formation of a Zn - porphyrin complex after the reaction between Zn and dithizone is described. This complex obeys the Beer - Lambert law, and is applied to the determination of Zn in biological materials. Results are reported for human serum, 106 to 214 μg per 100 ml, and for rat liver, 16 to 43 μg per gram. The sensitivity of the method is 26 μg per 100 ml.
D. B. Palmer

1424. **Simple micro-determination of Kjeldahl nitrogen in biological materials.** C. A. Lang (Div. of Medical Entomology, Dept. of Pathobiology, The Johns Hopkins Univ., Baltimore, Md., U.S.A.). *Anal. Chem.*, 1958, **30** (10), 1692–1694.—Digest the sample (< 5 mg of solid or 1 ml of liquid) in a test-tube (12·5 cm × 1·5 cm) at 310° or 320° for 1 hr. with 0·2 ml of a soln. prepared by mixing in order K_2SO_4 (40 g), selenium oxychloride (2 ml), H_2O (to produce 250 ml) and H_2SO_4 (250 ml). Allow to cool, dilute with H_2O, add Nessler reagent, and after 30 min. measure the extinction at 420 mμ or at 500 mμ (according to the amount of N). The range of the method is from 1 to 1000 μg of N. Good recoveries were obtained from lysine, uric acid and other refractory substances. The method is especially suited to routine analyses, because of the ease of manipulation and because specialised apparatus is not needed.
A. R. Rogers

1425. **The determination of blood ammonia; results in liver diseases.** N. Zöllner and P. Birk (Med. Poliklinik, Univ. München, Germany). *Klin. Wochschr.*, 1958, **36** (12), 570–574.—A modified method based on the Conway diffusion technique is described. The estimation is carried out on whole blood 5 min. after withdrawal; a greater or shorter lapse of time than this leads to erratic results. A significant rise in the NH_3 content was observed in liver diseases.
H. F. W. Kirkpatrick

1426. **Isotope dilution method for determination of nitrate in plant material.** H. Nömmik (Nat. Agric. Exp. Sta., Uppsala, Sweden). *Acta Agric. Scand.*, 1957, **7** (4), 389–394.—This method is free from interference by organic matter in the extract of the sample. The sample (0·1 to 1 g) is mixed with 10 ml of a standard ^{15}N-labelled nitrate soln., the amount of nitrate added being as nearly as possible equal to that in the sample. An aliquot of the filtrate from the mixture is transferred to one bulb of a two-limbed Rittenberg tube, the other bulb being charged with a 15% soln. of $TiCl_3$ in 5 *N* H_2SO_4. After evacuation of the apparatus, the two soln. are mixed and heated without delay. The ratio of ^{15}NO to ^{14}NO thus produced is determined in a mass spectrometer on the beams *m/e* 29 and 30. Appropriate measurements are also made for the calculation of the corrections due to the presence of small amounts of molecular nitrogen. The values obtained are ≃5% lower than those obtained by the phenoldisulphonic acid method, and of the same order of accuracy and reproducibility.
P. S. Arup

1427. **Semi-micro determination of bromides. Application to physiological fluids.** D. Kaplan and I. Schnerb (Res. Lab., Dead Sea Works, Ltd., Jerusalem, Israel). *Anal. Chem.*, 1958, **30** (10), 1703–1705.—The method of van der Meulen has been modified to allow of the determination of 10 μg of Br^- in organic materials without a prior ashing process. The maximum error is ±3%. *Procedure*—Prepare a soln. from urine or blood by removal of proteins with tungstic acid (for blood only), pptn. of AgBr, reduction of the ppt. with zinc and dil. acid, and filtration. Heat this soln. with 4% H_3BO_3 soln. (5 ml) and 0·3 *N* NaOCl (2·5 ml) at 80° to 90° for 15 min., add 25% formic acid soln. (0·5 ml) and cool. Add 5% KI soln. (2 ml), 2 *N* HCl (4 ml) and 0·25% starch soln. (0·5 ml) and after 3 min. titrate with 0·0002 *N* or 0·0004 *N* $Na_2S_4O_3$. Perform a blank titration.
A. R. Rogers

1428. **The estimation of iodine in biological materials: a modification of the method of Ellis and Duncan.** K. Rodgers and D. E. Poole (Dept. of Biochem., Univ. of Oxford, England). *Biochem. J.*, 1958, **70** (3), 463–471.—The method of Ellis and Duncan for the determination of protein-bound iodine in serum (*Anal. Abstr.*, 1954, **1**, 532) is considerably modified for the determination of mμg amounts of iodine in natural waters, milk and urine. Modified factors include the temp. during

the digestion of the sample, the amounts and types of the reagents added during the distillation of the iodine and the nature of the reagents used for trapping the iodine. The I^- obtained are determined by a modification of the method of Lein and Schwartz (*Brit. Abstr. C*, 1952, 82) which is based on the catalytic action of I^- on the reduction of Ce^{4+} by As_2O_3. The reaction is carried out at room temp. and the reduction is measured spectrophotometrically at 363 mμ. Chloride, Br^- and amounts of $F^- < 50$ μg per 10 ml do not interfere. Larger amounts of F^- partly inhibit the catalytic reaction.

J. N. ASHLEY

1429. **Rapid test for detection of certain iodine-containing contaminants in serum.** A. Grassmann and G. F. Grassmann (Grace Lab., 5909 Ridge Ave., Philadelphia, Pa., U.S.A.). *Clin. Chem.*, 1958, **4** (4), 296–299.—Serum is mixed with Na_2CO_3 soln. and heated in an oven at 215° to 220° for 10 min. The cooled soln. is tested by the arsenous acid - ceric sulphate reaction for high iodide content.

H. F. W. KIRKPATRICK

1430. **Serum iron determinations. Corrections for the bathophenanthroline and dipyridine [dipyridyl] procedures.** H. L. Rosenthal, M. L. Pfluke and L. Jud (Dept. of Path., Rochester Gen. Hosp., N.Y., U.S.A.). *Clin. Chem.*, 1958, **4** (4), 290–295.—Serum controls in which the serum is extracted with the solvent alone are essential to correct for interference by serum pigments. Results given by different methods become comparable when this precaution is taken.

H. F. W. KIRKPATRICK

1431. **Chemical determination of trace elements in biological material. XIII. Application of an extraction method to the simultaneous polarographic determination of iron, zinc and manganese in plant ash.** Katsumi Yamamoto (Chem. Dept., Fac. of Sci., Tohoku Univ., Katabiracho, Sendai). *Japan Analyst*, 1958, **7** (6), 343–346.—Jones's extraction method for Zn and Mn (*cf. Anal. Abstr.*, 1954, **1**, 2555) was modified to enable Fe and Cu to be determined simultaneously. A dil. HCl soln. of plant ash (*cf. Anal. Abstr.*, 1957, **4**, 718) is adjusted to pH 5·6 and extracted with $CHCl_3$ (3 × 5 ml) in the presence of cupferron soln. (5%, 3 ml); the extract is evaporated to dryness with H_2SO_4, HNO_3 and HCl, dissolved in HCl and submitted to polarography in 1·5 *M* Na acetate containing 0·08 *M* EDTA (pH 6·2) for the determination of Fe and Cu. Manganese and Zn are extracted with $CHCl_3$ containing Na diethyldithiocarbamate (Jones, *loc. cit.*) and the extract is evaporated to dryness with H_2SO_4, HNO_3 and HCl and dissolved in H_2O (10 ml) containing SO_2. An aliquot (*e.g.*, 1 ml) is mixed with 0·5 *M* LiCl (1 ml), and neutralised with LiOH to produce 6 ml of an aq. soln. of pH 6·2 for the polarographic determination of Zn and Mn.

K. SAITO

1432. **Polonium urinalysis.** C. A. Krebs and G. H. Whipple (Univ. of Rochester, N.Y., U.S.A.). *U.S. Atomic Energy Comm.*, Rep. UR-501, 1957, 14 pp.—For routine urine analysis, a copper disc (1 in. diam., 0·01 in. thickness) is prepared by immersion in a series of acid baths. The dried disc is hung in the urine sample and the liquid is stirred with a motor-driven glass propeller. Spontaneous exchange of Po proceeds for 2 hr. at room temp. The discs are then rinsed in H_2O, dried and counted in an α-scintillation counter.

K. R. C.

1433. **Determination of ethylenediaminetetra-acetic acid (EDTA) in urine and serum.** D. C. Smith and S. C. Tompsett (Northern Gen. Hosp., Edinburgh, Scotland). *J. Clin. Path.*, 1958, **11** (4), 365–366.—Urine is treated with $NiSO_4$ and NH_3, and then the excess of Ni not combined with the EDTA is pptd. with dimethylglyoxime soln. The filtrate is digested with H_2SO_4 and H_2O_2 and the Ni is then determined colorimetrically in the digest with dimethylglyoxime. Serum is deproteinised with $NiSO_4$ - NaOH, the filtrate is digested, and the Ni determined as for urine.

H. F. W. KIRKPATRICK

1434. **Gas-chromatographic analysis of alcohol and certain other volatiles in biological material for forensic purposes.** J. E. Fox (State Toxicol. Lab., Dept. of Pharmacol., Univ. of Washington, Seattle). *Proc. Soc. Exp. Biol. Med.*, 1958, **97** (1), 236–237.—A method for quant. micro-determinations of some volatile compounds from biological distillates that are of toxicological interest is presented. By fractional distillation of 1 to 3 ml of blood and gas-chromatographic analysis of the distillate in glycol columns, blood ethanol concn. were estimated to an accuracy within 5 mg per 100 ml and to a sensitivity of 10 mg per 100 ml in the presence of methanol, formaldehyde and putrefied blood. Microgram quantities of H_2S, ether, acetone, acetaldehyde, $CHCl_3$ and CCl_4 were also identified in aq. soln. *Procedure*—Pipette 1 to 5 ml of whole blood, urine or tissue extract into a 250-ml distilling-flask containing 25 ml of water, 3 ml of 50% sodium tungstate and 5 ml of *N* H_2SO_4. Pass the vapour through a heated fractionating column for 1 hr. Collect 20 to 25 ml of distillate in an ice-cooled receiver. *Gas chromatography*—The apparatus used was a Perkin-Elmer Fractometer model 154B set at full sensitivity in conjunction with a Leeds and Northrup Speedomax recorder with 5 mV full-scale sensitivity and a chart speed of 12 in. per hr. Inject a 0·1-ml or a 0·05-ml aliquot of the distillate into one of the two glycol columns with a 0·25-ml tubercular syringe. Determine the identity of the ethanol and other separated components by adding the suspected substance to the distillate and re-running the sample to see if the peak height in question is increased. Separated components can be quant. assayed by direct calibration of the column.

B. P. BLOCK

1435. **Polarographic determination of small amounts of morphine in blood and plasma.** K. Milthers (Copenhagen Univ., Denmark). *Acta Pharm. Tox., Kbh.*, 1958, **15** (1), 21–28.—In the method described, the sample is deproteinised with uranyl chloride and the supernatant fluid after centrifugation is acidified and autoclaved at 120° for 30 min. The soln. is then saturated with $NaHCO_3$ and extracted with $CHCl_3$ - *iso*propyl alcohol (3:1). The solvent extracts are distilled to dryness and the residue dissolved in *N* HCl is treated with nitrite for the polarographic determination of 2-nitrosomorphine. As little as 10 μg of morphine in 5 or 10 ml of blood may be determined with a recovery of 96 ± 5%. Half of any morphine injected intravenously was found to disappear from the blood stream within a few minutes.

W. H. C. SHAW

1436. **Comparison of new chemical method of determining isonicotinoyl hydrazide [isoniazid] in serum, with microbiological assay.** N. F. Poole and A. E. Meyer (Biochem. Res. Lab., Veterans

Admin. Hospital, Kerrville, Texas). *Proc. Soc. Exp. Biol. Med.*, 1958, **98** (2), 375–377.—The serum or plasma is deproteinised with 4 vol. of ethanol, the ppt. is centrifuged off, and aliquots of the supernatant liquid, corresponding to 1 ml of sample, are taken. These are mixed with 0·5 ml of 0·4% 1-fluoro-2:4-dinitrobenzene soln. in ethanol, and 0·1 g of borax, and heated at 80° for 5 min., in screw-capped tubes. The reaction mixture is decanted from any excess of borax, and the colour is read at 500 mμ. Standards, covering a range from 0·0 to 10·0 μg, are prepared from isoniazid-free plasma or serum. There is good agreement with microbiological assay methods, and the results are available the same day, instead of after several weeks.

D. B. PALMER

1437. **A simple clinical method for the determination of Salazopyrin (Azulfidine) [sulphasalazine] in serum.** L. E. Böttiger (Dept. of Clin. Biochem., Karolinska Sjukhuset, Stockholm, Sweden). *Scand. J. Clin. Lab. Invest.*, 1958, **10** (1), 108–109.—Use is made of the strong orange colour of sulphasalazine in alkaline soln. Difficulty arising from the colour of the serum itself is overcome by acidifying one portion, which is then used as a blank in colorimetric measurements. No significant difference in the extinction of serum at pH 11 and pH 1·3 has been found, confirming the validity of the acidified blank. In this way estimations can be carried out on jaundiced or haemolysed sera. A straight-line relation between concn. of sulphasalazine and extinction holds up to 15 mg per 100 ml (at 455 mμ) and recoveries of 88 to 99% have been obtained.

D. W. Moss

1438. **Micro-estimation of intact phenylmercury compounds in animal tissue.** V. L. Miller, D. Lillis and E. Csonka (Western Washington Exp. Sta., Puyallup, Wash., U.S.A.). *Anal. Chem.*, 1958, **30** (10), 1705–1706.—For urine, boil the sample (5 or 10 ml containing 5 to 20 μg of phenylmercury acetate) under reflux with *N* NaOH (20 ml). Cool, add 5% $KMnO_4$ soln. (12·5 or 25 ml according to the sample vol.) with thorough mixing, then 30% hydroxylamine sulphate - aq. NH_3 (1:1) (12·5 or 25 ml) and 30% ammonium sulphamate soln. (5 ml). Cool the mixture, add sufficient 12 *N* HCl under the surface of the liquid with vigorous swirling to lower the pH to $\gtrsim 1$ and cool again. Shake vigorously with purified $CHCl_3$ (11 ml) for 1 min. Wash the $CHCl_3$ layer by shaking with *N* HCl for 45 sec. and reject the washings. Shake the $CHCl_3$ layer for 30 sec. with 0·3 *N* acetic acid (25 ml) and a 0·0033% soln. of dithizone in purified $CHCl_3$ (1 ml), separate the $CHCl_3$ layer, dilute it to 11 ml and measure the extinction at 620 mμ. For kidney, liver, muscle or spleen, treat 1 g of sample as described above, but clarify the $CHCl_3$ layer by passage through a column of Hyflo Supercel before reaction with dithizone. For brain, the procedure is similar, but more vigorous treatment is necessary. The results are accurate to $\simeq \pm 1$ μg of phenylmercury compound.

A. R. ROGERS

1439. **New micro-method for the determination of sugars in medical laboratory practice.** F. I. Tokach. *Sb. Nauch. Rabot Zakapartsh. Obl. Klin. Bol'nitsy*, 1957, **1**, 87–93; *Ref. Zhur., Khim., Biol. Khim.*, 1958, (24), Abstr. No. 31,725.—*Procedure*—Blow out 0·2 ml of blood, taken from the patient's finger, into a test-tube containing 4 ml of a soln. of $ZnSO_4$ (0·45%) and 1 ml of NaOH (0·1 *N*). Heat on a boiling-water bath for 3 min., filter, and cool. Titrate the protein-free filtrate against 2 ml of a boiling alkaline soln. of $K_3Fe(CN)_6$ (100 mg per 100 ml) until the soln. is decolorised. Calculate the sugar content from the formula $C = 250/a(1{\cdot}04)$, where C = content of sugar in mg per 100 ml, a is the vol. in ml used up in titration, and 1·04 is the volumetric correction factor. This method is useful for the determination of sugar in various liquids.

K. R. C.

1440. **Determination of glucose, fructose and sucrose in plants.** Kh. N. Pochinok. *Biol. Fiziol. Rastenii*, 1958, (2), 27–33; *Ref. Zhur., Khim., Biol. Khim.*, 1958, (24), Abstr. No. 31,765.—A new method is described for the determination of glucose (**I**), fructose (**II**) and sucrose (**III**) when they are present together in plant-tissue extracts. The method is based on the different capacities of **I** and **II** to oxidise iodine in an alkaline medium. The total reducing sugars are determined in one portion of the extract by the Bertrand method. In another portion of the extract **I** is oxidised by iodine in the presence of NaOH. **II** is only slightly oxidised in these conditions as its degree of oxidation depends on the amount of **I** present in it. An empirical formula for calculating the amount of **II** present is given. The amount of **I** present is found by difference between the total reducing sugars and **II**. *Procedure for the determination of* **III**—This is based on the hydrolysis of the test soln. with HCl followed by a determination of the reducing sugar. The percentage content of **III** is obtained from the formula—**III** (%) = 0·95 ($S - U$), where S is the percentage content of total sugar (on conversion into **I**) and U is the percentage content of reducing sugars.

K. R. C.

1441. **Determination of 3-deoxyaldohexoses [and 3:6-dideoxyaldohexoses].** I. Fromme, O. Lüderitz, H. Stierlin and O. Westphal (Dr. A. Wander Res. Inst., Freiburg-Zähringen). *Biochem. Z.*, 1958, **330** (1), 53–58.—The oxidation of 3-deoxyaldohexoses and 3:6-dideoxyaldohexoses with sodium periodate yields 4-formyl-2-deoxy- and 4-formyl-2:5-dideoxy-aldopentoses, respectively, which are then determined by means of the Webb reaction (*cf.* Webb and Levy, *Anal. Abstr.*, 1955, **2**, 2194). This reaction, which is specific and sensitive, enables 5 to 200 μg of aldopentoses per ml to be determined and as little as 5 to 10 μg may be determined in the presence of other sugars.

D. B. PALMER

1442. **Detection of inositol and inositol diphosphate on paper chromatograms.** Y. Nagai and Y. Kimura (Inst. for Infectious Diseases, Univ. of Tokyo, Minato-ku). *Nature*, 1958, **181**, 1730–1731.—A simple, sensitive and reliable colour test, based on that of Fleury *et al.* (*cf. Anal. Abstr.*, 1954, **1**, 107), has been devised. The chromatogram is dipped in a soln. of 10 ml of conc. HNO_3 in 90 ml of ethanol and heated at 95° to 100° for 10 min. The paper is then exposed to NH_3 vapour for 1 to 2 sec. to remove excess of acid and then dipped in a mixture of *n*-butanol (40 ml), glacial acetic acid (10 ml), aq. 10% (v/v) Ba acetate soln. (10 ml) and $CaCl_2$ (0·5 g). After heating the paper for 4 to 5 min. at 95° to 100°, an orange colour due to Ba rhodizonate develops. The colour is sufficient to detect inositol in quantities above 8 μg, but below this concn. the colour must be intensified by spraying with 5% (w/v) $CaCl_2$ soln. in 50% ethanol and heating for 2 min. at 95° to 100°, when the orange colour changes through cherry red to rose pink; 1 μg of inositol can

then be detected. When the test is applied to the detection of inositol diphosphate, the ester is first hydrolysed by spraying the chromatogram with *N* HCl and heating at 95° for 4 min. This may be repeated twice to give sufficient hydrolysis. The procedure is then similar to that described above except that the treatment with HNO_3 - ethanol is repeated twice. The coloration is weaker than that given by free inositol but detection is easy. R_F values of inositol and inositol diphosphate in a solvent system of 62% (v/v) *tert.*-butyl alcohol containing 10% (w/v) trichloroacetic acid were 0·35 to 0·36 and 0·38 to 0·39, respectively, and in *iso*propyl alcohol - acetic acid - water (3:1:1, by vol.) were 0·19 to 0·20 and 0·13 to 0·15, respectively.

S. M. MARSH

1443. **Determination of rutin by the method of paper partition chromatography.** R. R. Rakhmanov. *Dokl. Akad. Nauk UzSSR*, 1958, (2), 51–54; *Ref. Zhur., Khim., Biol. Khim.*, 1958, (24), Abstr. No. 31,770.—The determination of rutin in plant-tissue extracts is carried out by means of an ascending technique. Good results were obtained with the following solvents—(*i*) *iso*amyl alcohol - methanol - water - formic acid (2:3:4:1); (*ii*) ethanol - water - acetic acid (3:6:1); (*iii*) *n*-butanol - ethanol - water - acetic acid (2:3:4:1) and (*iv*) methanol - water - formic acid (4:4:2). The best detecting agent was an ethanolic soln. of 2:6-dichlorophenol-indophenol (0·04%). R_F values for rutin from several plants are given.

K. R. C.

1444. **Comparative study of qualitative tests for ketones in urine and serum.** H. M. Free, R. R. Smeby, M. H. Cook and A. H. Free (Miles-Ames Res. Lab., Elkhart, Ind., U.S.A.). *Clin. Chem.*, 1958, **4** (4), 323–330.—A tablet test (Acetest) and a paper-strip test (Ketostix) are compared with standard Rothera and $FeCl_3$ procedures. Both of these proprietary tests are claimed to be more specific than, and equally as sensitive as, the standard tests. They are also suitable for detecting ketones in serum and plasma, and the tablet test will detect ketonaemia in whole blood.

H. F. W. KIRKPATRICK

1445. **Method for determining the phytol content of plants.** O. Hromatka, W. Bröll and L. Stentzel (Univ. Vienna, Austria). *Monatsh. Chem.*, 1958, **89**, 116–125.—For the determination of phytols in plant material the unsaponifiable lipids must be removed. The treatment adopted for preparing leaf extract was as follows. Leaves from *Aesculus hippocastanum* (1970 g) were dried at 70°, broken up, and put through a fine sieve. The 750 g of dried material was exhaustively extracted with 96% ethanol in a Soxhlet apparatus, the ethanol being replaced several times. The extracts were evaporated to 1 litre, 80 g of NaOH was added, and the mixture was heated under reflux on a water bath for 3 hr. After cooling, 3 litres of H_2O was added. The soln. was extracted 11 times with light petroleum (boiling-range 35° to 50°). The combined extracts were evaporated on a water bath, dried at 100° and 12 mm (Hg) to constant wt. (yield 23·9 g per litre). Part of the dried material (23·9 g) was dissolved in 100 ml of benzene which was distilled off and the residue dissolved in 5 ml of light petroleum. This soln. was transferred to an alumina column (35 mm × 17 mm) previously saturated with light petroleum, and a mixture of light petroleum - diethyl ether (3:1) was added. The coloured zone was mechanically removed and eluted with methanol - diethyl ether (3:1). The soln. was concentrated and placed in a tube (20 cm × 1 cm) having a 2-cm bulb on the end, evaporated to dryness (10 mm Hg) and the residue distilled under high vacuum. A light oil was collected at a bath temp. of 110° to 150° and 0·001 mm Hg. The distillate was taken up in 25 ml of benzene, 0·4 g of 4-phenylazophenyl *iso*cyanate was added, the mixture was refluxed in a moisture-free atmosphere for 6 hr., and the phytol determined by the colorimetric method.

CHEM. ABSTR.

1446. **Determination of coumarin in the presence of sterols.** J. R. Clopton (Dept. of Chem., Univ. of Colorado, Boulder). *J. Agric. Food Chem.*, 1958, **6** (6), 457–459.—Methods of determining coumarin involving a colour reaction with diazotised *p*-nitroaniline are inaccurate when applied to certain plant materials (*e.g.*, sweet clover) that contain sterols, for these give the same colour reaction as coumarin with this reagent. In the method proposed for the determination of coumarin in sweet clover seeds, the ground seeds are moistened to allow enzymic liberation of bound coumarin, the dried meal is extracted with 95% ethanol, and the coumarin content is measured spectrophotometrically at 275 mμ. The coumarin content was found to be 2·13%, compared with 2·30% by the usual method which includes sterols, and 0·88% for meal allowed to stand several months after grinding.

M. D. ANDERSON

1447. **Study of the tricarboxylic acid cycle by the method of partition chromatography.** Yu. A. Filimonov. *Trudy Voen. Med. Akad.*, 1957, (76), 23–27; *Ref. Zhur., Khim., Biol. Khim.*, 1958, (24), Abstr. No. 31,705.—Ascending chromatograms run on paper were used to determine acetic acid, malic acid, fumaric acid (**I**), citric acid and succinic acid (**II**). The keto acids were converted into their hydrazones and measured photometrically. Calculations were made by reference to a standard curve for each acid. **I** and **II** were detected in homogenates prepared from rat liver and kidney. **I, II** and oxaloacetic acid (**III**) were detected in urine. Pyruvic acid, **III** and α-oxoglutaric acid were determined in blood plasma. Chromatography can be combined with gasometric methods. After giving streptomycin, an accumulation of **III** and a reduction in the rate of respiration were observed. The preparation of the hydrazones of the acids, the solvents and the homogenates is described.

K. R. C.

1448. **Fluorimetric determination of gibberellic and gibberellenic acids in fermentation products, commercial formulations and purified materials.** F. Kavanagh and N. R. Kuzel (Antibiotics Mfg and Development Div. and Control Div., Eli Lilly and Co., Indianapolis). *J. Agric. Food Chem.*, 1958, **6** (6), 459–463.—Gibberellic acid is converted by 85% H_2SO_4 into a substance with blue fluorescence, and may thus be determined fluorimetrically after chromatographic separation on a column of $KHCO_3$, and elution with methyl cyanide, or directly on methanolic soln. of fermentation products, process samples, etc., by correcting for gibberellenic acid. This compound is included in the determination, but has little or no biological activity; it occurs in concn. up to 4% in crystalline gibberellic acid, 10% in fermentations, and higher in mother liquors obtained in the purification of gibberellic acid. It can be measured spectrophotometrically at 254 mμ; ketones and other interfering substances can be

removed by extraction of the gibberellenic acid first into *n*-butanol and then into a buffer of pH 7·5.
M. D. ANDERSON

1449. **Determination of urea in urine.** I. S. Rolzman. *Lab. Delo*, 1958, (4), 35–40.—Details are given of a technique in which the urease method is carried out in a diffusion vessel of the Conway type made of paraffin wax. W. ROUBO

1450. **Note on urea estimation by diacetyl monoxime.** J. T. Wearne (Royal Perth Hosp., W. Australia). *J. Clin. Path.*, 1958, **11** (4), 367.—In the method of Rosenthal (*Anal. Abstr.*, 1956, **3**, 1443) complete reaction is attained in 10 min. by heating at a steam pressure of 15 lb.
H. F. W. KIRKPATRICK

1451. **Chromatographic determination of creatine phosphate and of creatine.** M. Bistocchi (Ist. di Chim. Biol., Univ., Perugia, Italy). *Boll. Soc. Ital. Biol. Sper.*, 1957, **33**, 1782–1785.—The method described is a modification of that of Epshtein and Fomina (*Biokhimiya*, 1950, **15**, 321). The solvent chosen for a one-dimensional ascending technique on Whatman No. 1 paper is 2:4-lutidine - water (65:35). The experiment is allowed to continue for 20 to 22 hr. at a constant temp. of 20° to avoid changes in the saturation of the solvent which cause "tailing" of the spots. The chromatogram is dried at 110° for 1 hr. and is then sprayed with a mixture of saturated picric acid soln. and 10% NaOH soln. (4:1). Distinct spots are developed by creatine phosphate, creatine and various other Jaffé-positive substances liable to occur in extracts of animal tissues. After drying, the spots are subjected to photometric analysis, with a Photovolt model 501a apparatus and a green filter 525. A standard curve is made with the use of creatine phosphate or creatine soln., 0·01 *M* in 10% trichloroacetic acid, adjusted to pH 7·4 with NaOH. A table of R_F values shows that creatine and its phosphate can be clearly separated from glycocyamidine, and α-oxoglutaric, oxaloacetic, pyruvic and acetoacetic acids. Glycocyamine has an R_F value close to that of creatine. These two substances can be distinguished by the fact that the glycocyamine which changes to glycocyamidine does not develop its full colour until after heating for 3 hr. at 110° whereas all the other substances acquire their max. colour within 1 hr. of heating at the same temp. It is claimed that the method can be used for the determination of 0·5 μg.
P. HAAS

1452. **Application of high-voltage electrophoresis to the quantitative determination of metabolites.** W. Thorn, W. Isselhard and K. Irmscher (Inst. of Normal and Pathological Physiology, Univ. of Cologne). *Biochem. Z.*, 1958, **330** (5), 385–399.—The method described is suitable for the quant. determination of small amounts of free creatine, creatine phosphate, and inorganic phosphorus in organ extracts. The buffer used is a mixture of pyridine, 100 ml, glacial acetic acid, 6 ml, and water, 894 ml, and has a pH of 6·23 at 18°. Whatman No. 1 paper is the supporting medium, and the separation is performed at 1° to 3° by application of 60 V per cm for 90 to 100 min. Under these conditions the metabolites mentioned above are well separated from other phosphorus compounds present. Methods for the qual. and quant. determination of the separated compounds are given, the former by a series of dipping or spray reagents, the latter by elution and photometric assay of the eluate. Results reported include the R_F values of compounds present in organ extracts, levels of the various metabolites found, and the fact that the value of "labile phosphate" plus "bound creatine" corresponds to the creatine phosphate present. It is also shown that the losses by this method are 2% for stable metabolites and 4·5% for labile metabolites, when compared with results of the direct determination of these substances. The advantages of using high-voltage electrophoresis are (*i*) reduction in time, (*ii*) that the use of low temperatures protects labile compounds, and (*iii*) that creatine phosphate can be determined as one fraction and not by difference. D. B. PALMER

1453. **Spectrophotometric determination of total nucleic acids.** A. S. Spirin (Inst. Biochem., Acad. Sci., Moscow, USSR). *Biokhimiya*, 1958, **23** (5), 656–662.—A critical survey of known methods for the determination of nucleic acids is made. A modified spectrophotometric method is recommended. *Procedure*—Cover the preparation (5 to 500 mg of nucleoproteins, protein fractions, etc.) with 0·5 *N* $HClO_4$ (5 to 10 ml) and heat on a boiling-water bath for 20 min. Cool, centrifuge, and measure the u.v. absorption of the supernatant liquid at 270 mμ and 290 mμ against a control of pure 0·5 *N* $HClO_4$. The concn. of nucleic acid is expressed in micrograms per ml of soln. and is equal to the difference in extinction at 270 mμ and 290 mμ divided by 0·19. K. R. C.

1454. **Fluorimetric determination of adrenaline and noradrenaline in tissues.** A. Bertler, A. Carlsson and E. Rosengren (Dept. Pharmacol., Univ. Lund, Sweden). *Acta Physiol. Scand.*, 1958, **44** (3–4), 273–293.—After extraction of tissues by $HClO_4$ (0·4 *N*), the extracts are adjusted to ≃pH 4 with K_2CO_3, and the pptd. $KClO_4$ is centrifuged. An aliquot of the extract is adsorbed on a column (20 sq. mm × 12 mm) of Dowex 50 (Na^+), a strong cation-exchange resin. After rinsing the column with water, the adsorbed adrenaline and noradrenaline are eluted with *N* HCl (8 ml), and are differentially estimated by the fluorimetric method of Euler and Floding [*Acta Physiol. Scand.*, 1955, **33** (Suppl. 118), 45, 57], slightly modified. Fluorescence readings at 540 mμ are proportional to the adrenaline and noradrenaline content of the extracts when activating wavelengths of 455 mμ and 410 mμ, respectively, are used. The recovery figures compare favourably with those obtained when other adsorbents are used. D. G. MOSS

1455. **Simultaneous fluorimetric determination of adrenaline and noradrenaline in plasma. I. Fluorescence characteristics of adrenolutine and noradrenolutine and their simultaneous determination in mixtures.** G. Cohen and M. Goldenberg (Columbia Univ., New York). *J. Neurochem.*, 1957, **2**, 58–70.—Absorption spectra and fluorescence spectra are given for alkaline soln. of adrenolutine (**I**) and noradrenolutine (**II**). The fluorescence spectra were studied with both a filter fluorimeter and spectrofluorimeter. The peak fluorescence for **I** was at 520 to 525 mμ and that for **II** was at 510 to 515 mμ. The relative fluorescence of **II** compared to **I** was greatest in the 360 to 375-mμ region and much less in the regions near 340 mμ or 390 to 410 mμ. Details of apparatus and a discussion are given for a method of determining adrenaline and noradrenaline simultaneously. CHEM. ABSTR.

1456. **The reaction of adrenaline with potassium mercuric thiocyanate. Identification of the resulting adrenochrome by spectroscopy and paper chromatography.** J. Morvay, J. Császár and M. Almásy (Pharm.-chem. Inst., Univ., Szeged, Hungary). *Z. anal. Chem.*, 1958, **162** (3), 187–193.—The pink-red colour obtained by reaction of adrenaline with $K_2Hg(SCN)_4$ (*cf.* Salgó *et al.*, *Anal. Abstr.*, 1956, **3**, 2548) is due to the formation of adrenochrome.
A. R. ROGERS

1457. **Colorimetric method for determination of urinary porphyrins.** T. C. Chu and E. J.-H. Chu (Immaculate Heart College, Los Angeles, Calif., U.S.A.). *Anal. Chem.*, 1958, **30** (10), 1678–1680.—Adsorb the porphyrins from soln. of pH 3·5 on to talc, esterify overnight with 5% H_2SO_4 in methanol, dilute and extract into ethyl acetate. Evaporate to dryness, transfer to a chromatographic column of Hyflo Super-Cel and separate by development with $CHCl_3$ - light petroleum (boiling-range 30° to 60°) (1 : 2) (*cf. J. Biol. Chem.*, 1957, **227**, 506). Elute the individual fluorescent bands with $CHCl_3$ and determine spectrophotometrically by direct measurement at 500 or 405 or 625 mμ. Calculate with the aid of a calibration curve. The recovery is ≃95%.
A. R. ROGERS

1458. **Determination of unesterified fatty acids in normal human plasma.** A. Svanborg and L. Svennerholm (Med. Clin. II, Sahlgren's Hosp., Gothenburg, Sweden). *Clin. Chim. Acta*, 1958, **3** (5), 443–449 (in English).—Total lipids are extracted with methanol - $CHCl_3$, and contaminants are removed by phase partition. Phospholipids are then removed by chromatography on silicic acid and the fatty acids are titrated. Values found in normal individuals are given.
H. F. W. KIRKPATRICK

1459. **Determination of total lipids, cholesterol and phospholipids in cerebrospinal fluid.** E. Roboz, W. C. Hess, R. R. DiNella and W. Cevallos (Georgetown Univ. Med. Sch., Washington, D.C., U.S.A.). *J. Lab. Clin. Med.*, 1958, **52** (1), 158–162.—Lipids are extracted from the sample (10 ml) by shaking with $CHCl_3$ - methanol (2 : 1) at 85° to 90°. After centrifugation, the aqueous phase is removed and the solvent layer transferred quant. to a second tube for further aqueous extraction of non-lipid material. Total lipids are then determined colorimetrically in the purified extract by reaction with $K_2Cr_2O_7$ in conc. H_2SO_4 at 100° for 30 min. After dilution and cooling of the soln., the extinction is measured at 580 mμ. Calibration is with serum lipids over the range 10 to 200 μg. Cholesterol and its esters in an aliquot of the extract are separated and purified by chromatography on an alumina column, followed by elution and colorimetric determination in glacial acetic acid with a $FeCl_3$ - conc. H_2SO_4 reagent. The method is sensitive to 10 μg of cholesterol. Phospholipids are determined on another aliquot of the extract by wet-oxidation and colorimetric determination of phosphate with an ascorbic acid - molybdate reagent. As little as 0·15 μg of lipid P can be measured.
W. H. C. SHAW

1460. **Circular chromatography of phospholipids.** R. F. Witter, G. V. Marinetti, L. Heicklin and M. A. Cottone (Dept. of Biochem., Univ. of Rochester School of Medicine and Dentistry, Rochester 20, N.Y., U.S.A.). *Anal. Chem.*, 1958, **30** (10), 1624–1625.—Octanol - lutidine - acetic acid (18 : 1 : 2), $CHCl_3$ - lutidine - acetic acid (4 : 6 : 1), 3-methylbutan-2-one - acetic acid (10 : 1) and especially 2 : 6-dimethylheptan-4-one - acetic acid (6 : 1) are good solvents for the circular chromatography of phospholipids on Whatman No. 1 paper. Apply the sample containing 3 to 30 μg of phospholipid in benzene - *iso*amyl alcohol (1 : 1) (4 to 20 μl), develop at 21° to 23° for 1 or 2 hr. (or for 5 hr. with the first solvent-system), allow to dry, wash with H_2O, dry again and detect the separated compounds as described previously (*cf. Anal. Abstr.*, 1958, **5**, 197).
A. R. ROGERS

1461. **Studies on phospholipids. III. Determination of choline.** L. W. Wheeldon and F. D. Collins (Dept. of Biochem., John Curtin Sch. of Med. Res., Austral. Nat. Univ., Canberra). *Biochem. J.*, 1958, **70** (1), 43–45.—A micro colorimetric method is described for the determination of choline in lipids. It depends on hydrolysis of the lipid, pptn. of the choline in the hydrolysate by molybdophosphoric acid, reduction of the ppt. with $SnCl_2$, and determination of the extinction of the resulting blue soln. absorptiometrically with Ilford 608 filter. The amount of choline is then ascertained from a standard graph. Serine and ethanolamine do not interfere if their concn. is <20 μmoles per 0·5 ml. The presence of reducing sugar has no effect. The results agree with those obtained by the Reinecke salt method.
J. N. ASHLEY

1462. **Studies on phospholipids. IV. Determination of ethanolamine and serine.** F. D. Collins and L. W. Wheeldon (Dept. of Biochem., John Curtin Sch. of Med. Res., Austral. Nat. Univ., Canberra). *Biochem. J.*, 1958, **70** (1), 46–49.—The colorimetric method, which depends on a differential colour reaction, involves treatment of the lipids with 1-fluoro-2 : 4-dinitrobenzene, complete removal of excess of the reagent, hydrolysis of the dinitrophenyl lipids, and determination of the resulting dinitrophenylethanolamine and dinitrophenylserine by the colour reaction which does not involve their separation. Hydrolysis is effected with ethanolic *N* HCl at 100° for 3 hr. (whilst the mixture is shielded from light) followed by hydrolysis in *N* HCl. After evaporation, the hydrolysis residue is dissolved in a mixture of dimethylformamide, ethanol and *n*-butylamine and, after addition of tetramethylammonium hydroxide, the extinctions at 393 mμ and 500 mμ are measured. Equations are given for the calculation of the amounts of each of the components from these results.
J. N. ASHLEY

1463. **Determination of α-amino-acid nitrogen in urine.** C. Sobel, R. J. Henry, N. Chiamori and M. Segalove (Bioscience Lab., Los Angeles 64, Calif.). *Proc. Soc. Exp. Biol. Med.*, 1957, **95**, 808–813.—Results obtained for urine by the copper phosphate, naphthaquinone and gasometric - ninhydrin methods are compared and a modification of the photometric copper phosphate method for determination of α-amino acid and nitrogen in urine is presented. The specificity of the copper phosphate and naphthaquinone methods is improved by preliminary isolation of the amino acids on an ion-exchange column of Dowex 50-X8 (200 to 400 mesh, analytical grade, H form). Acidify 10 ml of urine to pH 1 to 2 with *N* HCl and pass through the column. Wash the column with two 1-ml aliquots and one 3-ml aliquot of 0·01 *N* HCl, then with water until the eluate is about pH 5. Elute with *N* NaOH. After about 3 ml of eluate has appeared,

collect 10 ml in a graduated centrifuge tube. *Procedure*—For greatest accuracy, or if much NH_3 is present, aerate the eluate for 30 min. Transfer 2·5 ml to a centrifuge tube; add 2·5 ml of water, one drop of thymolphthalein indicator and 6 *N* HCl dropwise until the indicator is decolorised, followed by *N* NaOH until the indicator just turns blue. Prepare a reagent blank by treating 5 ml of water with indicator and *N* NaOH in a similar tube. Prepare a standard with 2·0 ml of standard amino-acid soln. (0·268 g of glycine, 0·525 g of glutamic acid and 1 g of Na benzoate in 200 ml of water; add 5 ml of conc. HCl then water to 500 ml), 3·0 ml of water, one drop of indicator and *N* NaOH to a colour change. To each tube add 5·0 ml of a copper phosphate suspension, stopper and shake for 5 min. Centrifuge, and filter through paper. Dilute 1 ml of filtrate to 25 ml with water. Transfer 2·0 ml of each diluted filtrate to a test-tube, and add 0·1 ml of diethyldithiocarbamate reagent (40 mg of Na diethyldithiocarbamate in 2 ml of water, and filter) and 30 ml of *iso*propyl alcohol and mix. Read the extinctions of the unknowns and standard against the reagent blank at 435 mμ. B. P. BLOCK

1464. **Modification of the method for revealing amino acids on paper chromatograms by the use of isatin.** A. N. Boyarkin. *Fiziol. Rastenii*, 1958, **5**, 86–87; *Ref. Zhur., Khim., Biol. Khim.*, 1958, (23), Abstr. No. 30,041.—Amino acids were revealed on paper chromatograms by the use of isatin and an additional treatment with $MgSO_4$ was suggested (*Ref. Zhur., Khim., Biol. Khim.*, 1957, Abstr. No. 5727). Sodium silicate replaces $MgSO_4$ with advantage and considerably increases the sensitivity of the reaction between isatin and amino acids. The characteristic colours obtained by the use of isatin in old and new methods are described for 5 amino acids. K. R. C.

1465. **Correlation of R_F values and distribution coefficients in amino-acid chromatography.** W. M. McCord and G. H. Nelson (Dept. of Chem., Med. Coll., S. Carolina). *Proc. Soc. Exp. Biol. Med.*, 1958, **97** (1), 210–212.—The distribution coefficients of 19 amino acids between the two phases of a phenol - water mixture were determined at various pH values and temperatures. The R_F values were calculated and correlated statistically with the R_F values determined by paper chromatography, with the same developing system. A significant relationship was shown, and it was concluded that all variables should be standardised to obtain reproducible R_F values. D. B. PALMER

1466. **The "test-tube" method [for amino acids].** G. Gorbach (Tech. Hochschule, Graz, Austria). *Fette, Seif., Anstrichmitt.*, 1958, **60** (5), 364–366.—Improvements in the technique of determining amino acids by chromatography on short strips of paper in test-tubes (Rockland and Dunn, *Science*, 1949, **109**, 539) are described, and the method is extended to the separation of fatty acids. In order to obtain a high concn. of test substance at the point of deposition, a metal strip with apertures of 3-, 4- and 5-mm is used; with the paper held under the heated strip, the test soln. is deposited from a special capillary pipette at the centre of an aperture. Because of the rapid evaporation of the solvent, the spot remains concentrated in a small area. For the separation of fatty acids, the conditions are those described by Kaufmann and Nitsch (*Anal. Abstr.*, 1955, **2**, 2557; 1957, **4**, 278). E. HAYES

1467. **Rapid paper-chromatographic method for quantitative determination of tryptophan.** H. R. Roberts, M. G. Kolor and W. Bucek (Res. and Development Div., National Dairy Products Corp., Oakdale, L.I., N.Y., U.S.A.). *Anal. Chem.*, 1958, **30** (10), 1626–1627.—Tryptophan may be separated from other common amino acids by horizontal chromatography for 2 hr. at 60° with collidine - borate buffer of pH 9·0 (1:1) on Whatman No. 1 paper, and determined by measurement of the colour produced with ninhydrin reagent. The average recovery from 9 quant. separations was 98%, with a coeff. of variation of ±2·9%. The procedure has been applied to the determination of the tryptophan content of α-casein following alkaline hydrolysis. A. R. ROGERS

1468. **An identity test for iodinated derivatives of tyrosine and thyronine, particularly tri-iodothyronine and thyroxine.** P. Z. Anthony and J. E. Geever (Baxter Lab. Inc., Morton Grove, Ill.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1958, **47** (6), 394–395.—Dissolve the specimen (20 mg) in 95% ethanol (50 ml) with the aid of dil. HCl if necessary. Mix a 2-ml aliquot with 95% ethanol (4·5 ml) and 17% NaCl in *N* HCl soln. (12·2 ml) and add freshly prepared 1% $NaNO_2$ soln. (2·5 ml). Allow to stand in the dark for 20 min. and add aq. NH_3 soln. (*d*, 0·880) to produce 25 ml. Iodotyrosine and 3:5:3′-tri-iodothyronine give an orange colour; di-iodotyrosine and thyroxine give a pink colour; dihydroxyphenylalanine gives an amber colour; tyrosine, 3:5-di-iodothyronine and tryptophan remain colourless. This test is an application of the reaction of Kendall and Osterberg (*J. Biol. Chem.*, 1919, **40**, 265). A. R. ROGERS

1469. **Amperometric titration of sulphydryl [mercapto] groups at a rotating platinum electrode.** H. Burton (Nat. Inst. Res. Dairying, Reading Univ., England). *Biochim. Biophys. Acta*, 1958, **29** (1), 193–201.—An investigation is made into the influence of pH on the titration of mercapto compounds with $AgNO_3$ or $HgCl_2$ in aq. NH_3 - NH_4NO_3 or in tri(hydroxymethyl)methylamine buffers. The titrations of cysteine, reduced glutathione, mercaptosuccinic acid and of β-lactoglobulin are studied in detail. Results differ significantly from theoretical values under certain conditions, which are discussed, and it is concluded that the titrations are not necessarily specific for mercapto groups even with simple thiols. W. H. C. SHAW

1470. **Determination of mercapto compounds in micro and ultra-micro amounts of tissue.** V. A. Yakovlev and Yu. M. Torchinskiĭ (Lab. of Histochem., Acad. Med. Sci., Moscow, USSR). *Biokhimiya*, 1958, **23** (5), 755–759.—A special vessel is described for the amperometric micro-titration of mercapto groups (in biological fluids and tissue homogenates) which is also a micro-homogeniser. The vessel contains a cone-shaped depression into which fits a glass pestle fused to a glass tube projecting above the vessel. A platinum electrode (25 mm long and 0·5 mm thick) passes up this tube through a mercury contact. Another glass tube is fused to one side of the vessel and contact is made between its agar gel contents and the titration soln. in the vessel across an agar bridge with minimum diameter of 0·1 to 0·22 mm. An $AgNO_3$ soln. (10^{-3} *M*) is run in from an ultramicro-burette of the horizontal type and capacity 30 μl. The results of amperometric macro- and micro-titrations on the same material are compared and the difference

varies from 2·4 to 3·8%. Amounts of material containing 1·5 to 2 × 10^{-3} mole of mercapto groups can be analysed, such as histological sections from the cerebral cortex of the cat. K. R. C.

1471. **The distribution of ergothioneine in blood as determined by a new method of estimation.** P. C. Jocelyn (Univ. of Edinburgh, Scotland). *Biochem. J.*, 1958, **70** (4), 656–660.—The method, which is easy to carry out and appears to be specific for ergothioneine in biological samples, depends on the liberation of trimethylamine when the compound is heated with 50% w/v aq. KOH at 100° for 1 hr. The trimethylamine is aerated into a soln. of picric acid in benzene and the extinction of the resulting soln. is determined spectrophotometrically at 410 mμ. There is a linear relation between extinction and concn. of trimethylamine up to 5 mg per 100 ml. Methylamine and NH_3, if present, are removed by prior aeration through Nessler soln. Dimethylamine gives a positive reaction but the colour produced is only 20% of the intensity for the same wt. of trimethylamine. Choline and betaine liberate no trimethylamine under the standard conditions. For the determination of trimethylamine in the presence of ergothioneine, K_2CO_3 is used instead of KOH in the decomposition reaction when only the free trimethylamine is liberated. J. N. Ashley

1472. **Comparison of methods for the determination of total protein in cerebrospinal fluid and other very dilute solutions.** H. P. Rieder (Psychiat. Univ.-Klinik, Basle, Switzerland). *Clin. Chim. Acta*, 1958, **3** (5), 455–470.—The Kjeldahl, sulphosalicylic acid and Folin copper methods, and direct measurements in u.v. light, are investigated. The Folin copper method is recommended for routine use. H. F. W. Kirkpatrick

1473. **Fractionation of Bence-Jones protein by starch-gel electrophoresis.** F. V. Flynn and E. A. Stow (Dept. of Clin. Path., Univ. Coll. Hosp., London). *J. Clin. Path.*, 1958, **11** (4), 334–338.—Several sera and urines from cases of myeloma showing one abnormal component by paper electrophoresis were found to contain more than one abnormal protein when run in starch gel. On starch the abnormal proteins in urine rarely correspond with those of the serum even when they do so on paper. Resolution on starch is better than on paper and has diagnostic value in myeloma.
H. F. W. Kirkpatrick

1474. **Improved separation of serum proteins in paper electrophoresis. A new electrophoresis buffer.** T. Aronsson and A. Grönwall (Dept. of Clin. Chem., Univ. Hospital, Uppsala, Sweden). *Scand. J. Clin. Lab. Invest.*, 1957, **9** (4), 338–341.—A buffer is described which gives an improved and more constant separation of serum proteins into the following nine fractions—pre-albumin, albumin, three α-components, three β-components, and γ-globulin. The buffer soln. used has the following composition —tri(hydroxymethyl)methylamine (60·5 g per litre) (0·5 *M*), EDTA (6·0 g per litre) (0·021 *M*), and boric acid (4·6 g per litre) (0·075 *M*), the pH being 8·9. Electrophoresis is carried out for 16 hr. at a potential gradient of 6·5 V per cm, the resulting protein bands are stained with Amido black 10B, and evaluated by direct photometry. As supporting media, Whatman 1, S. & S. 2043B acetylated, and cellulose acetate paper are used with comparable results. For the cellulose acetate paper it is necessary to use the buffer at 1·3 times the strength given, and a potential gradient of 4·5 V per cm.
D. B. Palmer

1475. **Procedure for recovery of proteins from electropherogram layers.** T. Wieland, G. Pfleiderer and H.-L. Rettig (Inst. of Org. Chem., Univ. Frankfurt). *Angew. Chem.*, 1958, **70** (11), 341–343.—In the method described, electrophoresis is first carried out on starch. The section immediately in front of the protein band is then replaced by insertion of a glass-powder preparation supported on Cellophane foil. Electrophoresis is continued to drive the protein into the glass powder. Elution from this medium can then be made with small amounts of solvent with a recovery of over 90%.
H. F. W. Kirkpatrick

1476. **Small-scale membrane-filter electrophoresis and immuno-electrophoresis.** J. Kohn (Queen Mary's Hosp., Roehampton, London, England). *Clin. Chim. Acta*, 1958, **3** (5), 450–454.—An apparatus suitable for micro-electrophoresis is described. Samples of 0·1 to 10 μl can be separated giving neat and distinct patterns.
H. F. W. Kirkpatrick

1477. **Determination of the carbohydrate content of separated serum-protein fractions.** H. Südhof (Med. Univ. Klinik, Göttingen, Germany). *Klin. Wochschr.*, 1958, **36** (11), 536–538.—Dried paper strips after electrophoresis are cut lengthwise to give duplicates, one portion being stained for protein and the other for carbohydrate. The strip for carbohydrate determination is immersed in periodic acid reagent, then washed briefly, and placed in a bath of decolorised para rosaniline. The colour is developed with formaldehyde - aq. NH_3 soln. and, after being washed clear with ethanol and acid ethanol, the paper is dried, rendered transparent and scanned. Some results are tabulated and discussed. H. F. W. Kirkpatrick

1478. **Differentiation on paper of proteins and acid mucopolysaccharides by means of combined specific stains.** J. Heremans and J. P. Vaerman (Univ. de Louvain, Hosp. St. Pierre, Belgium). *Clin. Chim. Acta*, 1958, **3** (5), 430–434.—Two combined staining techniques for chromatographic and electrophoretic strips are described. In the first, Alcian blue followed by azocarmine, with intermediate washing and drying, stains proteins pink and acid mucopolysaccharides blue. In the second, Mucicarmine and bromophenol blue, used similarly, stain proteins blue and acid or neutral mucopolysaccharides pink. The first method is more sensitive and specific.
H. F. W. Kirkpatrick

1479. **Seromucoid (mucoprotein) determination in experimental animals.** H. E. Weimer and F. A. Quinn (Sch. of Med., Univ. of Calif., Los Angeles, U.S.A.). *Clin. Chim. Acta*, 1958, **3** (5), 419–422.—It is recommended that a final concn. of 0·6 *N* $HClO_4$ be employed in the initial pptn. and in the isolation of seromucoid fractions, as changes in concn. alter both the chemical composition and the amount of the fraction. H. F. W. Kirkpatrick

1480. **Determination of lipoproteins by paper electrophoresis.** P. Mainat, W. Appel and E. F. Tuller (New England Deaconess Hosp., Boston, Mass., U.S.A.). *Clin. Chem.*, 1958, **4** (4), 304–310.—The paper strips from electrophoresis are dried at room temp. for a minimum of 4 hr. and are then

stained in a saturated soln. of Sudan black B in a mixture of methanol, *iso*propyl alcohol and H_2O (3:3:4) for 2 hr. at 40°. The strips are washed in 30% *iso*propyl alcohol (6 successive 5-min. baths), dried on glass plates, and scanned. A higher total uptake of dye, especially by α-lipoproteins, is obtained, and the results are reproducible.

H. F. W. KIRKPATRICK

1481. **Pre-staining procedure for electrophoretic study of serum lipoproteins.** A. A. Wilcox, P. T. Wertlake, M. I. Haley and J. E. Peterson (Dept. Biochem. Intern. Med., College of Medical Evangelists, Loma Linda, Calif.). *Proc. Soc. Exp. Biol. Med.*, 1958, **98** (4), 718–721.—A method for staining lipoproteins with acetylated Sudan black, before electrophoresis, is described. This method saves time and reagents, gives greater contrast between bands and background, requires no rinsing of the stained strips, and gives more reproducible results than post-staining methods. Determinations on sera from persons of various ages and sex are reported, and the results compare favourably with those obtained by other methods of lipoprotein estimation.

D. B. PALMER

1482. **Spectroscopic data for steroids subjected to Zak colour reaction.** F. Bischoff and J. G. Turner, jun. (Santa Barbara Cottage Hosp. Res. Inst., Calif., U.S.A.). *Clin. Chem.*, 1958, **4** (4), 300–303.—The reaction products of 18 steroids treated with the H_2SO_4 - $FeCl_3$ reagent in glacial acetic acid were examined in the range 320 to 700 mμ. The results are tabulated and discussed.

H. F. W. KIRKPATRICK

1483. **Phosphoryl chloride enhancement of the fluorescence of steroids in sulphuric acid.** J. C. Touchstone, R. A. Keisman, A. F. Marcantonio and J. W. Greene, jun. (School of Med., Univ. of Pennsylvania, Philadelphia, U.S.A.). *Anal. Chem.*, 1958, **30** (10), 1707.—The fluorescence of certain steroids in H_2SO_4 can be increased considerably by the addition of about 30% of $POCl_3$. This treatment causes little or no change in the wavelength of the max. of the emitted light when compared with that of the steroid in H_2SO_4 alone. Results obtained indicate that the intensity of fluorescence is proportional to the concn. of the steroid subject to the usual limitations of fluorimetry.

K. A. PROCTOR

1484. **A method for the determination of plasma corticosteroids.** F. T. Brayer (Univ. of Rochester, N.Y., U.S.A.). *U.S. Atomic Energy Comm.*, Rep. UR-513, 1957, 13 pp.—Free plasma corticosteroids in microgram quantities or less were determined by descending paper chromatography. The papers were developed in a benzene - formamide system for 40 min. and then transferred to a $CHCl_3$ - formamide system for 30 min. The corticosteroid was revealed by staining with a 0·25% aq. soln. of blue tetrazolium (4 ml) and 0·1 *M* NaOH (1 ml). The stained spot was cut out and eluted with formamide for 1·5 hr. in a chromatography jar which contained only $CHCl_3$ in the reservoir. The eluate was evaporated and an ethanolic soln. of blue tetrazolium and tetramethylammonium hydroxide soln. were added. After 35 min. in the dark, the reaction was stopped by an ethanolic soln. of HCl and the extinction at 510 mμ was measured. The recovery of corticosterone added to plasma was 97%.

K. R. C.

1485. **Practical procedure for estimation of corticosterone or hydrocortisone [cortisol].** R. H. Silber, R. D. Busch and R. Oslapas (Merck Inst. for Therap. Res., Rahway, N.J., U.S.A.). *Clin. Chem.*, 1958, **4** (4), 278–285.—The simple method described is based on the measurement of the fluorescence with 30 *N* H_2SO_4 at 530 mμ with an exciting wavelength of 470 mμ. Specificity is limited, but an increase or decrease in adrenocortical hormones in a small vol. (0·5 ml) of plasma can be demonstrated.

H. F. W. KIRKPATRICK

1486. **Ultra-micro method for determination of amylase activity in blood serum.** J. R. Close and H. V. Street (Wythenshawe Hosp., Manchester, Lancs., England). *Clin. Chim. Acta*, 1958, **3** (5), 476–479.—The method previously described (*cf.* Street and Close, *Anal. Abstr.*, 1957, **4**, 2346) is modified for use with 10 μl of serum.

H. F. W. KIRKPATRICK

1487. **Measurement of enzymatic amylolytic activity. Addendum to group A: Viscosimetric determination of amylase.** H. Wildner and G. Wildner (Ireks Forschungsinst. für Gärungswissenschaft, Kulmbach, Germany). *Brauwissenschaft*, 1958, **11** (4), 86–89.—A full description is given of Belderok's procedure (*cf. Anal. Abstr.*, 1957, **4**, 684), which eliminates interference by β-amylase and other accompanying enzymes, and can be applied to the detection of incipient (visually undetectable) germination in single grains of wheat.

B. Addendum: Determination of activity of amylases in malt. H. Wildner and G. Wildner. *Ibid.*, 1958, **11** (4), 89.—A description is given of Blom's method [*cf. Getreide u. Mehl*, 1955, **5**, 107; *Brauerei, Wiss. Beil.*, 1958, (1)].

P. S. ARUP

1488. **Colorimetric method for the quantitative determination of plasma catalase activity.** G. B. Dabkin and M. D. Glantz (Dept. of Chem., Brooklyn Coll., N.Y., U.S.A.). *Clin. Chem.*, 1958, **4** (4), 316–322.—The method described is based on the Prussian blue colour produced by reaction of residual H_2O_2 with ferricyanide and ferric gum ghatti (prep. described).

H. F. W. KIRKPATRICK

1489. **Determination of prothrombin in blood.** L. T. Margolina and B. V. Lyutrovnik. *Lab. Delo*, 1958, (4), 15–18.—The method of Quick for the determination of prothrombin in blood is not a sensitive one. The sensitivity, however, has been improved by diluting blood with a physiological solution. Such a dilution of blood does not in any way affect any of the factors responsible for the coagulation of blood.

W. ROUBO

1490. **Serum-trypsin determination in pancreatic disease.** G. L. Nardi (Harvard Med. Sch., Boston, Mass., U.S.A.). *J. Lab. Clin. Med.*, 1958, **52** (1), 66–69.—The method is based on the hydrolysis of α-benzoyl-L-arginine amide hydrochloride in the presence of trypsin to benzoyl-L-arginine and NH_3. The liberated NH_3 is determined by a modification of the Conway micro-diffusion technique. The method is specific for trypsin among the serum enzymes and is accurate (duplicate determinations) to ±50 units. Results >100 units are considered abnormal, and the significance of high results is discussed in relation to pancreatic diseases.

W. H. C. SHAW

1491. **Quantitative determination of pancreatic protease activity.** Z. Placer (Forschungsinst. f.

Volksernährung, Prague, Czechoslovakia). *Klin. Wochschr.*, 1958, **36** (11), 538.—A rapid method is proposed in which the soluble copper salts of liberated amino acids are measured colorimetrically. *Procedure*—To the substrate (5 ml) at 38° add the test soln. (0·5 ml), incubate at 38° for 15 min., add NaOH soln. (5 ml) and copper reagent (5 ml), shake and filter, and measure the absorption of the filtrate at 640 mμ. Prepare a blank similarly without warming or incubation. Units of activity may be expressed as mg of Cu in 10 ml of *N* aq. NH_3 and read from a curve prepared with various dilutions of $CuSO_4.5H_2O$ in *N* aq. NH_3. Two sets of reagents are given—*A*(*i*) 2% casein in a mixture of 0·2 *M* $NaHCO_3$ (7 vol.) and 0·2 *M* Na_2CO_3 (3 vol.), pH 8·9, *A*(*ii*) 0·4 *N* NaOH, *A*(*iii*) 0·3 *M* $CuSO_4.5H_2O$ in 0·5 *M* H_3BO_3; *B*(*i*) 1% casein in 0·2 *M* $NaHCO_3$, pH 8·4, *B*(*ii*) 0·09 *N* NaOH, *B*(*iii*) 0·1 *M* $CuSO_4.5H_2O$. H. F. W. KIRKPATRICK

1492. **Solubilisation and assay of choline dehydrogenase.** G. Rendina and T. P. Singer (Henry Ford Hosp., Detroit, Mich., U.S.A.). *Biochim. Biophys. Acta*, 1958, **30** (2), 441–442.—The use of phenazine methosulphate as acceptor in the manometric assay of particulate and soluble preparations for choline dehydrogenase is recommended. The sample activity is estimated by extrapolation of results obtained at a series of dye concentrations to infinite dye concentration. W. H. C. SHAW

1493. **Fluorimetric method for measuring the activity in serum of the enzyme glutamic - pyruvic transaminase.** T. Laursen and P. From Hansen (Dept. of Clin. Chem., Rigshospitalet, Copenhagen, Denmark). *Scand. J. Clin. Lab. Invest.*, 1958, **10** (1), 53–58.—Pyruvate and glutamate are produced by the action of glutamic - pyruvic transaminase when serum is incubated for 10 min. at 37° with a substrate containing L-alanine and α-oxoglutarate. Lactic dehydrogenase, nicotinamide and reduced diphosphopyridine nucleotide (**I**) are also incorporated in the substrate. Pyruvate is converted into lactate by lactic dehydrogenase with oxidation of **I** to diphosphopyridine nucleotide (**II**), the amount of **II** formed being proportional to the amount of pyruvate present. **II** is determined by the fluorescence of its condensation product with ethyl methyl ketone; this compound is highly fluorescent and is stable for 24 hr. Possible interference by the inherent fluorescence of **I** is overcome by acidification, and the addition of nicotinamide prevents destruction of **II** by **II**-ase. Primary and secondary filters with max. transmission at 360 and 480 mμ, respectively, are used. Recoveries of 97 to 103% of added pyruvate are obtained. Duplicate estimations have a standard deviation of ±0·1 unit (98 duplicates) and normal values are 0·8 unit, standard deviation ±0·5 unit (94 estimations). A vol. of 0·2 ml of serum is required, although reduced quantities may be used. Optimum conditions of substrate and serum concn., pH and incubation time and temp. are discussed. Correlation with results of the Wroblewski and Cabaud colorimetric technique is not good; this is attributed to poor recoveries of pyruvate in the colorimetric method. D. W. Moss

1494. **Estimation of quinine oxidase activity in serum in the differential diagnosis of obstructive jaundice and hepatitis.** H. Baier (Städt. Ferdinand Sauerbruch-Krankenstalten Wuppertal-Elberfeld, Germany). *Klin. Wochschr.*, 1958, **36** (12), 569–570.—The enzyme is present in significant amount only in the liver and is not detectable in normal serum. In hepatitis and other diseases with liver damage a significant rise in activity occurs. In obstruction due to stones or malignant tumour the value usually remains below 4 units. *Procedure*—To 1 ml of serum add 3 ml of 0·066 *M* phosphate buffer soln. (pH 7·2), mix and add 1 ml of quinine hydrochloride soln. (25 mg dissolved in 100 ml of H_2O). Read the extinction in a 1-cm cell at 366 mμ after exactly 1 min. and again after a further 10 min. at room temp., against a blank prepared by mixing 0·9 ml of serum with 4·1 ml of buffer soln. One unit of activity is taken as an increase of 0·001 in the extinction under the test conditions. H. F. W. KIRKPATRICK

1495. **A simplified method for the determination of amino-acid amidases in tissue cultures.** L. R. Sabina (Univ. Nebraska, Coll. Agric., Lincoln, U.S.A.). *Proc. Soc. Exp. Biol. Med.*, 1958, **98** (4), 824–826.—A diffusion method for the estimation of the amino-acid amidase content of tissues grown *in vitro* is reported. The simple reaction flask used is described, and the method, which is rapid and precise, is applicable to other enzyme systems evolving ammonia. D. B. PALMER

See also Abstracts—**1505**, Determination of acetylcholine. **1572**, Determination of protein-bound iodine. **1581**, Coulometer for electrophoresis of proteins.

Pharmaceutical analysis

1496. **Application of the potentiometric method to the detection of quinine and codeine zones on paper chromatograms.** B. Zapiór and B. Śliwa (Dept. of Gen. Chem., Jagellonian Univ., Cracow). *Roczn. Chem.*, 1958, **32** (2), 397–402.—The method, introduced by Kamieński [*Rozpr. PAU*, 1949, **A74** (3), 7], consists in measuring the change in potential of the indicating electrode of the micro cell: Sb | 0·1 *N* KCl ‖ test soln. | Sb, as the electrode is applied to the chromatogram at intervals along its length. It detects 2·5 μg of codeine, is less sensitive for quinine, but is applicable to mixtures in which the ratio of quinine to codeine is up to 2:1 and also to mixtures containing a large excess of codeine. T. M. M.

1497. **A note on the detection of ephedrine by spot test.** F. Feigl and E. Silva (Lab. da Prod. Mineral, Min. da Agric., Rio de Janeiro). *J. Amer. Pharm. Ass., Sci. Ed.*, 1958, **47** (6), 460.—Mix the solid, or the dry residue from a drop of soln., with sodium bismuthate (≃20 mg) in a micro test-tube and heat. Hold over the end of the tube a piece of filter-paper moistened with a drop of a freshly prepared mixture of 20% aq. morpholine - 5% aq. sodium nitroprusside (1:1). Ephedrine (<5 μg) and compounds with a C_2H_5O- or $C_2H_5N<$ group give a blue spot on the yellow paper. Adrenaline (<10 mg) does not interfere. A. R. ROGERS

1498. **Oscillopolarographic characterisation of *Veratrum* alkaloids.** L. Molnár and K. Molnárová (Dept. Pharm. Chem. and Biochem., Chem. Inst. Acad. Sci., Bratislava, Czechoslovakia). *Chem. Zvesti*, 1958, **12** (5), 287–303.—The oscillopolarographic behaviour of *Veratrum* glycoalkaloids, esters and alkamines (jervine, rubijervine, *iso*rubijervine, protocevine, germine, cevagenine, cevine, *pseudo*jervine, cevadine, protoveratridine, veratridine, germerine, protoveratrine) in 2 *N* NaOH, *N* LiOH, *N* LiCl, *N* aq. NH_3 - NH_4Cl, *N* Na_2SO_4,

N H_2SO_4 and *N* HCl as supporting electrolytes has been studied with the use of the streaming- and dropping-mercury electrodes. Characteristic incisions of studied compounds are suitable for identification purposes; a list of values is given of depolarisation potentials in all the electrolytes used. The possibilities of the detection of jervine, rubijervine and *iso*rubijervine in mixtures are discussed. It has been found that the oscillopolarographic method is suitable for the study of the rate of hydrolysis of esters of *Veratrum* alkaloids.
J. ZÝKA

1499. **The chemical determination of cardiac glycosides and organic nitrates in pharmaceutical preparations.** A. Kurkela (Satamakatu 4 A 9, Helsinki, Finland). *Pharm. Acta Helv.*, 1958, **33** (6), 216–224.—The Baljet reaction (*Schweiz. Apoth-Ztg*, 1918, **56**, 89) with picrate is used to determine the glycoside content of pharmaceutical preparations of digitalis and squill glycoside. Standard curves using the appropriate glycoside or mixture are used for calibration. The method is usually accurate to within 2 to 3%. The organic nitrate content of glycerol trinitrate and erythritol tetranitrate are determined either colorimetrically with phenoldisulphonic acid or preferably by reduction of NO_3 to NH_3 and subsequent titration (*cf. J. Ass. Off. Agric. Chem.*, 1951, **34**, 716, and *Norges Apotek. Tidskr.*, 1946, **54**, 535). S. BAAR

1500. **A new phosphate complex salt of tetracycline.** M. A. Kaplan and F. H. Buckwalter (Bristol Lab. Inc., Syracuse, N.Y., U.S.A.). *Antibiot. & Chemother.*, 1958, **8** (7), 361–363.—The chemical and physical properties described include u.v. and i.r. absorption data. W. H. C. SHAW

1501. **Simultaneous determination of chlortetracycline (Aureomycin) and tetracycline in a mixture.** A. Sauciuc, W. Unterman, G. Caraculacu and R. Toma (Inst. Chem. Pharm. Res. Iaşi, Romania). *Rev. Chim., Bucharest*, 1958, **9** (6), 339–341.—Total tetracyclines are determined photometrically (*cf.* Levine *et al.*, *Brit. Abstr. C*, 1950, 18) after boiling 1 to 3 ml of soln. of the antibiotic with 0·1 to 0·3 ml of conc. HCl on a water bath for 5 min. The individual antibiotics are determined by heating with 0·2 *M* Na_2PO_4 for 2 min. on a water bath. Most of the activity of the chlortetracycline is destroyed, but the tetracycline is unaffected and is determined photometrically. By the use of a formula the proportions of each can be determined (*Cf.* Doskočil, *Anal. Abstr.*, 1957, **4**, 2773.)
H. SHER

1502. **Physico-chemical methods for the determination of antibiotics. IV. Colorimetric determination of biomycin [chlortetracycline].** L. B. Senyavina and B. P. Bruns (All-Union Sci.-Res. Inst. of Antibiotics, Moscow). *Zhur. Anal. Khim.*, 1958, **13** (5), 613–616.—Improvement is made in Levine's method (*Brit. Abstr. C*, 1950, 18) for the determination of chlortetracycline (**I**) by means of its conversion into the orange-yellow anhydrochlortetracycline. Take 1 ml (or more for dilute soln.) of the soln. of **I** in each of two 50-ml flasks. To the first add 5 ml of 2 *N* HCl and to the second 5 ml of water. Place both flasks in a boiling-water bath for 3·5 min., cool rapidly in cold water, add 5 ml of 2 *N* HCl to the second (control) flask and dilute both soln. to vol. Measure the extinction of the first soln. at 430 mμ with the second as comparison soln. The difference in the extinctions is directly proportional to the concn. of **I** at concn. <1200 to 1300 μg per ml. The colour of the soln. is stable for 5 hr. If more than 1 ml of soln. is taken originally, the amount of HCl added must be increased so as to maintain the concn. of acid given above. The method is very specific and may be used for the determination of **I** in pure and industrial soln. It may be used for the analysis of culture liquids if the concn. of **I** is <50 μg per ml. The results obtained by the described method and by the microbiological assay method agree well if the culture liquid is inactivated in strongly acid (pH $\simeq 2$) or weakly alkaline soln. (For Part III see *Zhur. Anal. Khim.*, 1957, **12**, 262.) C. D. KOPKIN

1503. **Physico-chemical methods for the determination of antibiotics. V. Influence of various factors on the accuracy of the determination of streptomycin by the maltol method.** V. D. Kartseva and B. P. Bruns (All-Union Sci. Res. Inst. of Antibiotics, Moscow). *Antibiotiki*, 1958, **3** (5), 39–44.—The influence of the concn. of NaOH, and the temp. and time of heating, on the alkaline hydrolysis of streptomycin to form maltol, and the influence of concn. of H_2SO_4 and $(NH_4)_2SO_4.Fe_2(SO_4)_3$ in the colorimetric determination of the maltol, are studied. It is shown that, during the hydrolysis, two reactions take place, namely the formation and the decomposition of maltol. Increase of alkali concn. and temp. of heating increases the rates of both reactions. The formation of maltol is rapid and the max. amount is formed within 1 to 3 min. at a hydrolysis temp. of 100°. The decomposition reaction is slower, and by carrying out the hydrolysis at 60° with 0·5 to 2 *N* NaOH, or at 100° with 0·2 *N* NaOH, its rate is practically zero. These facts are confirmed by working with pure maltol. It is confirmed that 1 mole of streptomycin produces 0·75 mole of maltol. In the colorimetric determination of the maltol, variation of the H_2SO_4 concn. from 0·03 to 0·4 *N* alters the extinction by 15 to 30%; increase of $(NH_4)_2SO_4.Fe_2(SO_4)_3$ concn. from 4×10^{-3} millimole per ml to 32×10^{-3} millimole per ml changes the extinction by 15 to 18%. The extinction decreases by 9 or 10% within 30 min. of the formation of the colour. *Procedure*—Add 2 ml of 0·2 *N* NaOH to 10 ml of the streptomycin soln. containing 100 to 300 μg per ml, place in a boiling-water bath for 4 min., cool in running water for 3 min., add 8 ml of a 1% soln. of $(NH_4)_2SO_4.Fe_2(SO_4)_3$ in 0·55 *N* H_2SO_4 and measure the extinction exactly 3 min. after the addition. If the procedure is followed rigorously, accurate and reproducible results may be obtained. No interference is caused by the presence of Na, K, Li, Cs, Al, Ca and Mg at concn. of 0·05 to 0·5 *N*. C. D. KOPKIN

1504. **Paper chromatography of streptothricin antibiotics. Differentiation and fractionation studies.** M. I. Horowitz and C. P. Schaffner (Inst. of Microbiology, Rutgers, State Univ., New Brunswick, N.J., U.S.A.). *Anal. Chem.*, 1958, **30** (10), 1616–1620.—Circular paper chromatography with *n*-propanol - pyridine - acetic acid - H_2O (15:10:3:12) as solvent is preferred to ascending or descending paper chromatography for the separation of the peptide-like antibiotics related to streptothricin. Most of the antibiotic preparations examined showed the presence of several components.
A. R. ROGERS

1505. **Colorimetric determination of acetylcholine by the Hestrin reaction with hydroxylamine, and its applications to pharmacy.** D. Vincent, G. Segonzac

and M.-C. Vincent (Fac. de Méd. et de Pharm., Toulouse, France). *Ann. Pharm. Franç.*, 1958, **16** (3), 179–185.—The Hestrin reaction of acetylcholine with hydroxylamine to give acetohydroxamic acid which, on acidifying and adding $FeCl_3$, gives a red colour, is used quantitatively. *Procedure*—In three tubes are placed, respectively, 1 ml of a standard containing 1 mg of acetylcholine, 1 ml of acetylcholine soln. of unknown concn. and in the third tube 1 ml of water. To each is added 0·4 ml of hydroxylamine soln. (2·78 g in 20 ml of water and 40 ml of 3·5 *M* NaOH) and then, after shaking for 30 sec., 0·3 ml of 4 *M* HCl, 0·2 ml of 0·37 *M* $FeCl_3$ (in 0·1 *M* HCl) and 5 ml of water. The tubes are shaken carefully between each addition. The extinctions are measured at 520 mμ. A linear calibration curve is obtained and the error is <5%. The method is applied to determine the deterioration by hydrolysis of aged soln. of acetylcholine. Besides choline esters the colour reaction is given by a number of other compounds, which are mentioned.
E. J. H. Birch

1506. **Iodimetric determination of ascaridole and chenopodium oil.** H. Böhme and K. van Emster. *Arch. Pharm., Berlin*, 1958, **291** (6), 310–318.—Ascaridole liberates more than 2 equiv. of iodine probably owing to its reaction with HI to give *p*-menth-2-ene-1:4-diol which can oxidise further HI. The empirical relation between the amount of ascaridole (m) and ml of 0·1 *N* thiosulphate soln. used (n) is $m = An + Bn^2$, where A and B are constants depending on experimental procedure. In the method described, for m = 100 to 150 mg of ascaridole, A = 50 and B = 0·042. *Procedure*—Chenopodium oil dissolved in acetic acid is added to a mixture of KI soln., acetic acid and HCl at −1° to −3° and stirred in ice-cold water for 3 min. The flask is then held for 2 min. at room temp., some water is added and the mixture titrated by adding thiosulphate from a fully open burette until the soln. is decolorised. Excess of thiosulphate is then titrated with iodine.
M. H. Sawistowska

1507. **Non-aqueous assay for substituted barbituric acids.** S. W. Goldstein and D. F. Dodgen (Amer. Pharm. Ass. Lab., Washington, D.C.). *Drug Standards*, 1958, **26** (4), 113–115.—The following procedure is recommended after a comparison of six methods of non-aqueous titration. Dissolve the sample (200 mg) in dimethylformamide (20 ml) and titrate with 0·1 *N* Li methoxide in methanol-benzene (15:85), with thymol blue as indicator; stir magnetically and protect the soln. from atmospheric CO_2. Perform a blank titration.
A. R. Rogers

1508. **Determination of barbituric acid derivatives as mercury complexes.** C. O. Björling, A. Berggren, B. Willman-Johnson, A. Grönvall and B. Zaar (Res. Lab., Pharmacia Ltd., Uppsala, Sweden). *Acta Chem. Scand.*, 1958, **12** (5), 1149–1150 (in English).—Add 0·3% $Hg(NO_3)_2$ soln. (1 ml) to a soln. of the sample (50 to 250 μg) in H_2O (10 ml) and buffer at a pH of 8·0. Extract with an organic solvent (4 × 10 ml). Suitable solvents are $CHCl_3$ for the N-substituted compounds, amylobarbitone and 5-allyl-5-phenylbarbituric acid; $CHCl_3$ with 20% dioxan for phenobarbitone; $CHCl_3$ with 20% benzyl alcohol for allobarbitone, barbitone, cyclobarbitone and 5-allyl-5-*iso*propylbarbituric acid (aprobarbital). Filter through glass wool, add 0·0015% dithizone in $CHCl_3$ and dilute to 100 ml with $CHCl_3$. Measure the extinction at 605 mμ against a reagent blank. Certain hydantoins and cyclic imides of dicarboxylic acids interfere. The method is easily modified to allow the determination of as little as 2 μg of barbiturate.
A. R. Rogers

1509. **Quantitative anodic chronopotentiometry at a platinum electrode. Application to the sulpha drugs.** J. D. Voorhies and N. H. Furman (Princeton Univ., N.J., U.S.A.). *Anal. Chem.*, 1958, **30** (10), 1656–1659.—The results of this study indicate that the method is analytically useful over the 10^{-3} *M* to 10^{-4} *M* concn. range, and the results obtained had a coeff. of variation of about 1%.
K. A. Proctor

1510. **Colorimetric determination of chlorpromazine.** S. Farkas (United Pharmaceutical Factories, Budapest). *Magyar Kém. Foly.*, 1958, **64** (6), 209–211.—Chlorpromazine gives a pink colour reaction with tungstophosphoric acid, which is specific and follows Beer's law. A 20% soln. of dodecatungstophosphoric acid in *N* HCl (1 ml) is added to the dil. soln. of chlorpromazine (5 ml) containing 100 to 300 μg. The extinction is measured after 2 min. in a Pulfrich colorimeter against a blank, an S53 filter being used. The decomposition products, if present, may be observed with an S61 filter by the increased extinction. The method is used for the assay of tablets and injections.
G. Szabo

1511. **Amperometric determination of dimethylaminoacetylphenothiazine.** J. Blažek and Z. Stejskal (State Inst. for Drug Control, Prague). *Pharm. Zentralh.*, 1958, **97** (6), 255–257.—To determine dimethylaminoacetylphenothiazine (**I**) in tablets, finely powder the sample (containing 100 to 200 mg of **I**), add conc. HCl (1 ml), dilute with H_2O to 20 ml and titrate amperometrically with 0·01 *M* tungstosilicic acid at a potential of −0·65 V *vs.* the S.C.E. After each addition of reagent, stir for 3 min. and wait for 5 min. before reading the current intensity. The error is <−1·5%.
A. R. Rogers

1512. **Determination of individual components in "B complex" dragées.** Z. Kleflin and K. Šumanović ("Pliva" Pharm. and Chem. Works, Zagreb, Yugoslavia). *Croat. Chem. Acta*, 1958, **30** (3), 181–187 (in English).—The method involves selective extraction of the various components and their determination by physico-chemical methods. Thiamine hydrochloride is determined by dissolving the dragées in water, treating the acidified extract with diazotised *p*-aminoacetophenone in alkaline medium to give a red colour, extraction with xylene and photometric measurement of the extract. *p*-Aminobenzoic acid is extracted with warm ether, and titrated with 0·1 *M* $NaNO_2$. Nicotinamide is extracted with hot $CHCl_3$ and titrated with 0·1 *N* $HClO_4$ in dioxan to methyl red. Calcium pantothenate is extracted with water, the soln. is made alkaline with *N* NaOH and titrated with 0·1 *M* EDTA, with murexide as indicator. Riboflavine is extracted with 50% ethanol, treated with Denigès reagent and the colour determined photometrically. Pyridoxine hydrochloride is determined by titrating an aq. extract with 0·05 *N* $AgNO_3$ to give total HCl and subtracting the amount associated with thiamine as determined previously. Full experimental details are given.
S. M. Marsh

1513. **Determination of aromatics in medicinal paraffin.** K. A. Fischer, G. Brandes and W. Gohdes (Zentrallab., Dtsch. Erdöl A.-G., Hamburg, Germany). *Pharm. Ind.*, 1957, **19**, 293; *Erdöl u.*

Kohle, 1958, **11** (4), 261.—The proportion of the C present in the form of aromatic rings ($A\%$) is found from the max. extinction coeff. ($\log I_0/I$) at 250 to 270 mμ by the relation: $A = (\log I_0/I)/kcd$, where c is the concn. of the oil in the solution tested in g per litre, d is the cell length in cm, and k is the mean value of the max. extinction coeff. of several alkylbenzenes, each in a concn. giving $A = 1\%$ in a paraffin oil. Polycyclic condensed aromatics which absorb more strongly than benzene homologues are usually absent from medicinal paraffin. There is no relation between A and the intensity of fluorescence of an oil. A. R. PEARSON

1514. **Assay of certain ointments in non-aqueous solution.** S. M. Wang, H. W. Starr and R. J. Hoffman (Southern College of Pharmacy, Atlanta, Ga.). *Drug Standards*, 1958, **26** (4), 116–117.—A mixture of chlorobenzene and $CHCl_3$ (5:1) is used to dissolve ointment bases such as petrolatum, polyethylene glycol base or hydrophilic ointment base U.S.P. before non-aqueous titration. To assay ointments of ammoniated mercury, benzocaine or *n*-butyl *p*-aminobenzoate "picrate," dissolve the sample (4 g) in the mixed solvent (25 ml), add glacial acetic acid (50 ml) and titrate with 0·1 *N* $HClO_4$ in glacial acetic acid, with methyl violet as indicator. A. R. ROGERS

See also Abstracts—**1178**, Reactions of barbituric acid and phenazone with flavylium perchlorate. **1354**, Determination of ethanol in tinctures. **1360**, Determination of acetaldehyde in paraldehyde. **1361**, Determination of chloral hydrate. **1366**, Colorimetric determination of hexamine. **1368**, Determination of alkyl nitrites. **1399**, Standards for essential oils. **1435**, Determination of morphine in blood. **1436**, Determination of isoniazid in serum. **1437**, Determination of sulphasalazine in serum. **1438**, Determination of phenylmercury compounds in biological materials. **1537**, Spectrophotometric determination of vitamin A. **1538**, Chemical determination of vitamin D. **1539**, Determination of thiamine. **1566**, Microbiological determination of stilboestrol.

Food

Foods and food additives, beverages, edible oils and fats, vitamins.

1515. **A method for the determination of bran in flour.** W. L. Deatherage and M. M. McMasters (Northern Utilization Res. and Dev. Div., Peoria, Illinois, U.S.A.). *Cereal Chem.*, 1958, **35** (5), 380–392.—Flour is dispersed in *iso*propyl alcohol and treated with NaOH and water. Particles remaining on a micro-metallic filter after filtration are backwashed into a graduated centrifuge tube and their volume is measured after centrifuging. Recovery experiments show that approx. one-third of the bran is retained in this manner. The particles separate into two layers: white and brown. The volume of the particles and their dry weight are nearly linearly related. No relationship is found between the weight of total or of brown particles and the ash content of the flour. Some relationship (non-linear) is found between the weight of the brown particles and the Kent-Jones colour grade. J. V. RUSSO

1516. **Colorimetric determination of residual perchloroethylene [tetrachloroethylene] in fumigated wheat.** J. H. Brumbaugh and D. E. Stallard (Res. Centre, Diamond Alkali Co., Painesville, Ohio). *J. Agric. Food Chem.*, 1958, **6** (6), 465–467.—The Fujiwara colour reaction for halogenated compounds is not sensitive for tetrachloroethylene, and the colour fades rapidly. Residual tetrachloroethylene is determined colorimetrically in fumigated wheat by digesting the sample in 0·15 *N* H_2SO_4 under reflux, the condenser being held at 65° to retain the water; released fumigant is swept into pyridine absorbers by a current of air; the pyridine soln. is refluxed with addition first of aniline, and then of NaOH in methanol; an orange colour develops. The method is not specific for tetrachloroethylene; other halogenated compounds react, optimum reaction conditions varying with compound. The rate of disappearance of tetrachloroethylene from fumigated wheat is recorded. M. D. ANDERSON

1517. **Determination of choline in egg products, flour and noodles.** H. Salwin, M. D. Devine and J. H. Mitchell, jun. (Quartermaster Food and Container Inst. for the Armed Forces, 1819 West Pershing Road, Chicago, Ill.). *J. Agric. Food Chem.*, 1958, **6** (6), 475–479.—The total choline in food products, as a measure of egg content, is determined by extraction with abs. methanol, heating with $Ba(OH)_2$ to hydrolyse phospholipids, acidifying with glacial acetic acid to the phenolphthalein end-point, filtering, and pptg. choline as the reineckate, which is measured spectrophotometrically in acetone soln. at 530 mμ. Determinations on samples of dried whole egg and egg yolk, durum semolinas, and semolina - farina blends are reported. The method measures the total choline of the phospholipids, whether or not they have undergone hydrolysis, and is therefore independent of manufacturing conditions and storage history. M. D. ANDERSON

1518. **Comparative accuracy of small lactometers for determining the total solids of individual cow's milk.** D. E. Madden and J. R. Brunner (Mich. State Univ., East Lansing, U.S.A.). *J. Dairy Sci.*, 1958, **41** (6), 783–788.—A statistical study is made of the performance of a Watson and a Quevenne type lactometer and of the influence of fat content on the total solids calculated from the readings obtained. Results are compared with those obtained by gravimetric determinations on samples from 350 cows of five dairy breeds. Field use of the small Watson lactometer is recommended, provided that temp. and reading technique are controlled. W. H. C. SHAW

1519. **Some factors affecting turbidimetric methods for the determination of fat in milk.** J. D. S. Goulden (Nat. Inst. Res. Dairying, Reading Univ., England). *J. Dairy Res.*, 1958, **25** (2), 228–235.—Determination of the fat content of milk from measurements of the turbidities of the diluted milk at 1·2 μ is shown to be more accurate than the alkali-addition method in the visible region. The effects of breed and time of lactation on the results are studied. It is concluded that, although the max. deviation with a given breed corresponds to $\pm 0{\cdot}2\%$ in the fat concentration, errors up to 0·5% may arise in samples of herd milk according to the mixture of breeds and the proportion of cows in the early stages of lactation. W. H. C. SHAW

1520. **Determination of free fatty acids in milk.** D. R. Perrin and D. D. Perrin (Ruakura Animal Res. Sta., Dept. Agric., New Zealand). *J. Dairy*

Res., 1958, **25** (2), 221–227.—The extraction-titration method described gives recoveries from 63% for butyric to 97% for stearic acid; neither citric nor lactic acid at the levels present in fresh milk interfere. *Procedure*—To 10·0 ml of milk in a 50-ml stoppered centrifuge tube add 3 drops of 0·5% bromophenol blue and *N* H_2SO_4 to a greenish-yellow colour (usually 1 to 1·5 ml). Add 5 ml of 95% neutral ethanol, stopper the tube and shake vigorously for 1 min. Add 15 ml of an ether-light petroleum (boiling-range 30° to 60°) mixture (2:1), stopper, shake vigorously for 1 min. and centrifuge at 1500 r.p.m. for 5 min. To 10 ml of the supernatant layer add 10 ml of neutralised methanol and titrate to a greenish tinge with 0·01 *N* ethanolic KOH, with 1-naphtholphthalein as indicator. Carry out a blank determination with water. The difference in titration (ml) multiplied by 1·35 gives the concn. in millimoles of free fatty acid. Prepare the neutralised alcohols by adding 0·05 ml of 1% 1-naphtholphthalein solution to 10 ml and titrating with ethanolic KOH. W. H. C. SHAW

1521. **Rapid determination of milk salts and ions. I. Determination of sodium, potassium, magnesium and calcium by flame spectrophotometry.** V. R. Wenner (Nestlé Products, Vevey, Switzerland). *J. Dairy Sci.*, 1958, **41** (6), 761–768.—The sample of fresh (60 ml) or powdered (7·5 g) milk is diluted to 100 ml and casein is pptd. with 5 ml of *N* HCl. After 10 min. the pH is adjusted to 4·0 to 4·1 with *N* aq. NH_3 and the soln. is diluted to 150 ml. After filtering or centrifuging, 100 ml of the clear serum is passed (4 ml per min.) through a column (30 cm × 0·9 cm) of Dowex-50 resin (30 to 40 mesh, H form). The column is washed with water (3 × 10 ml) and then eluted with 3·5 *N* HCl (2 ml per min.). The first 3 ml of eluate is rejected and the following 50 ml containing all the cations is collected in a 50-ml flask. Individual cations are determined on suitable dilutions of this soln. by flame-photometric methods, with a spectrophotometer and photomultiplier calibrated with standards of similar ionic composition. The max. deviation of single determinations is ±2%. W. H. C. SHAW

1522. **Use of fluorescent materials for the indirect detection of antibiotics in milk.** R. E. Hargrove, R. J. Lehman and C. A. Matthews (U.S. Dept. Agric., Washington, D.C., U.S.A.). *J. Dairy Sci.*, 1958, **41** (5), 617–623.—The addition of a combination of fat-soluble fluorescein and sodium fluorescein to penicillin preparations intended for intramammary infusion is proposed as a rapid and satisfactory means for detecting antibiotics in milk. The marker is detectable visually for 48 hr. and under u.v. light for 96 hr. after treatment, and its excretion shows good correlation with that of penicillin. W. H. C. SHAW

1523. **Determination of allethrin residues in milk and meats.** D. B. McClellan and J. B. Moore (McLaughlin Gormley King Co., Minneapolis, Minn.). *J. Agric. Food Chem.*, 1958, **6** (6), 463–465.—Allethrin is determined colorimetrically in meat or milk by extraction with light petroleum (boiling-range 20° to 40°), removal of solvent, and reaction with HgO - H_2SO_4 reagent. Allethrin gives a red colour, and the chrysanthemum-monocarboxylic acid component of allethrin, in the free state, gives a pink to purple colour. Allethrin was not found in the milk of cows sprayed daily for three weeks with allethrin in oil, or in the muscle, heart, kidney, or fat of a female goat sprayed daily for five weeks; in both cases, concn. of allethrin were much in excess of those normally employed. M. D. ANDERSON

1524. **Phospholipids in New Zealand dairy products. I. Estimation of the total phospholipids and of lecithin, cephalin and sphingomyelin in butter.** A. K. R. McDowell (Dairy Res. Inst., Palmerston North, New Zealand). *J. Dairy Res.*, 1958, **25** (2), 192–201.—A modification of the Röse - Gottlieb method is described for the extraction of phospholipids from butter serum. Procedures for the determination of lecithin, cephalin and sphingomyelin in the extract are based on analyses for (*i*) total P found by digestion with 10 *N* H_2SO_4 and H_2O_2, and colorimetric determination with 1-amino-2-naphthol-4-sulphonic acid, (*ii*) soluble P found as in (*i*) on the filtrate obtained by trichloroacetic acid pptn. after hydrolysis with KOH, and (*iii*) choline determined by the reineckate method after KOH treatment. Lecithin is calculated from (*iii*) and the other compounds from (*i*) and (*ii*) after correction for lecithin P. The extraction of phospholipids with other solvent mixtures from butter serum before and after trichloroacetic acid treatment is studied and the differences in results are discussed.

II. Seasonal variations in the phospholipid content of butter and of milk and cream. A. K. R. McDowell. *Ibid.*, 1958, **25** (2), 202–214.—Mean results and their ranges are given for a 3-year study on milk, skim-milk, buttermilk, raw and pasteurised cream and butter. Average weighted results for phospholipids and for lecithin, cephalin and sphingomyelin in butter were 0·139, 0·041, 0·051 and 0·047%, respectively. W. H. C. SHAW

1525. **Determination and isolation of the non-volatile acids of pome fruits and a study of acid changes in apples during storage.** A. C. Hulme and L. S. C. Wooltorton (Ditton Lab., Larkfield, Maidstone, Kent, England). *J. Sci. Food Agric.*, 1958, **9** (3), 150–158.—A comprehensive scheme is described in which anion-exchange resins in their acid form and "gradient elution" (Hulme, *J. Exp. Bot.*, 1951, **2**, 298) are used. The scope of the method is illustrated by the quant. examination of a mixture containing 14 acids. Changes that occur in the peel and pulp of Bramley's Seedling apples on storage are investigated. These changes involve not only malic, citramalic and citric acids, but also the alicyclic quinic and shikimic acids, and the relationships between these acids in the fruit are discussed. H. B. HEATH

1526. **Ethylene metabolism in tomato fruit. II. Determination of total and carbon-14-labelled ethylene.** M. S. Spencer (Dept. of Biochem., Univ. of Alberta, Edmonton, Alta, Canada). *Canad. J. Biochem. Physiol.*, 1958, **36** (6), 595–601.—The concn. of ^{14}C-labelled compounds was determined in soln. Ethylene was absorbed from the air stream in 0·25 *M* $Hg(ClO_4)_2$ in 2 *M* $HClO_4$. Fifteen parts of this soln. were added to 85 parts of ethanediol. Stainless-steel planchettes, ringed with wax to avoid "creeping," were used. Total ethylene was measured manometrically with a specially modified Warburg apparatus. A gas-flow counter was used to determine ^{14}C-labelled ethylene. As the presence of ethanediol only increased the time necessary for the complete liberation of ethylene but not the overall yield, the same sample could be used for total ethylene and ^{14}C-labelled ethylene. Replicate counts gave a maximum variation of 2·4%. The method is suitable for the analysis of 1 or 2 tomatoes or their equivalent. S. BAAR

1527. **New simple process for determination of benzoic acid in foods.** P. Spanyár, E. Kevei and M. Kiszel (ForschInst. f. Konserven-, Fleisch- und Kälteindustrie, Budapest). *Z. LebensmittUntersuch.*, 1958, **107** (2), 118–124.—The benzoic acid is extracted with ether, then nitrated, and the resulting 3:5-dinitrobenzoic acid in acetone - abs. ethanol soln. (1:1) is mixed with a little NaOH. The stable blue - violet colour produced is a measure of the quantity of benzoic acid. The mean error of measurement by model experiments was ±0·9% and for five different foodstuffs ±2 to ±6·8%. The method is specific and the separation processes in most cases are simple and time saving.
S.C.I. Abstr.

1528. **Paper-chromatographic isolation and determination of chlorogenic acid [in coffee].** J. Erkama and K. Kauppila (Biochem. Inst., Univ. Helsinki, Finland). *Suomen Kem., B*, 1958, **31** (1), 82–84 (in German).—Chlorogenic acid (**I**) and caffeic acid (**II**) from coffee were separated by using as solvent *n*-butanol - glacial acetic acid - water (4:1:5) on Whatman No. 1 paper for 26 hr. at 19°. The spots were revealed with a mixture of equal vol. of 10% acetic acid and 1% $NaNO_2$ soln. The R_F values obtained for **I** (yellow spot) and for **II** (red spot) were 0·50 and 0·80, respectively. After spraying the paper with NaOH soln. the colours changed to red (spot of **I**) and to yellow (spot of **II**). For the quant. determination of **I**, the corresponding spots were extracted with *iso*propyl alcohol and the concn. measured spectrophotometrically at 327 mμ. The precision of the method is within ±5%. The content of **I** in raw coffee was found to be 7·0% and no free **II** was observed in this material.
E. Sjöström

1529. **Kiln heating and malt analysis.** W. J. Klopper (Brauerei d'Oranjeboom, Rotterdam, Holland). *Brauwissenschaft*, 1958, **11** (7), 154–157.—The pH of Congress wort obtained from malt kilned by direct heating by coke is ≃0·2 less than that of malt kilned by hot air. This difference has little effect on the yield of extract, but higher yields of sol. N (by 5 to 6%) are obtained at the lower pH. On acidifying the mash from pH 5·8 or 6·0 to 5·4 or 5·5, the extract is increased by ≃1%, the sol. N is increased by ≃10%, whilst the Hartong saccharification value at 45° is considerably increased in relation to the values obtained at 65° or 80°. The importance of defining the pH at which the determinations are to be carried out is stressed. As the results obtained in actual practice are influenced by several factors (*e.g.*, the pH of the brewing water), the current analytical procedures are of limited value.
P. S. Arup

1530. **Determination of sulphydryl [mercapto] groups [in beer].** F. Knorr (Versuchsanstalt für Bierbrauerei der Bayer, Landesgewerbeanstalt, Nuremberg, Germany). *Brauwissenschaft*, 1958, **11** (7), 158–159.—For this determination, the method of conductimetric titration with 0·001 *N* $AgNO_3$ is preferred. The beer, after passage over a Lewatite exchanger and concentration by dialysis, is titrated in a cell with a rotating platinum electrode, in connection with a calomel electrode. Beer is found to contain 25·1 to 28·6 μg, and colloidal chill haze 5·0 to 7·0 μg of mercapto groups per 100 ml and 100 g, respectively.
P. S. Arup

1531. **Comparative paper-chromatographic identification of wines.** R. J. Peltonen, M. Kitunen and H. Suomalainen (ForschLab. Staatl. Alkoholmonopols, Helsinki, Finland). *Z. LebensmittUntersuch.*, 1958, **107** (1), 15–20.—By the method described the changes in amino-acid composition during fermentation and ripening in wines were followed. The amino-acid chromatograms of the same wines are easily reproducible. In the same wines of different years, deviations in the total concn. of amino acids are shown, but the proportions remain the same. Different kinds of wine show distinct differences in total amino-acid content. The proportions of various amino acids, *e.g.*, alanine, proline, etc., and the presence or absence of phenylalanine form a good evaluation basis.
S.C.I. Abstr.

1532. **Iodine value of the unsaponifiable matter in the differentiation of olive from other oils.** L. Frontero (Soc. R.I.O., Imperia, Italy). *Olii Min.*, 1958, **35** (6), 227–228.—The iodine value of the unsaponifiable matter, extracted with light petroleum, is higher (93 to 119) for olive than for other oils such as tea seed (54) or peanut (49) and may be used for differentiation. Similarly, esterified products from olive oils give higher values (79 to 89) than products from animal fats (37 to 42). (*Cf.* Bolton and Williams, *Analyst*, 1930, **55**, 5.)
L. A. O'Neill

1533. **Correlation of chromatographic absolute loss determinations with the A.O.C.S. cup refining method in soya-bean oil.** E. Sipos (Central Soya Co. Inc., Decatur, Indiana, U.S.A.). *J. Amer. Oil Chem. Soc.*, 1958, **35** (5), 233–236.—This correlation was examined statistically, with degummed and un-degummed soya-bean oil. In the chromatographic method, a tube (20 mm × 400 mm) filled with activated alumina and an ether solvent are used. Good correlation is obtained for samples with higher than 1% chromatographic losses; below this level, correlation is not good, owing to the nature of the cup refining method. Results on 88·5% of the total samples show 1% differences between duplicates. The degumming of oils to levels below 1% chromatographic losses is not always indicated by the cup loss method.
G. R. Whalley

1534. **Horizontal paper chromatography of fats and lipids. The higher fatty acids.** H. Sulser (Lab. Eidg. Gesundh. Bern). *Mitt. Lebensmitt. Hyg., Bern*, 1958, **49** (4), 264–272.—The fatty acids isolated conventionally are dissolved in $CHCl_3$ and an equal volume of undecane is added. Aliquots (≃ 1 mg) are applied to thin tongues of paper which also act as wicks. The paper is impregnated with liquid paraffin before use (*cf. Ibid.*, 1956, **47**, 149; 1957, **48**, 117, 248). The saturated acids are located as their copper soaps and the unsaturated acids are oxidised with periodate and permanganate and the oxidation product detected with a benzidine reagent. The method described has been used for the identification of saturated and unsaturated fatty acids in lard, palm-kernel oil and coconut oil. The following acids were separated—stearic, palmitic, myristic, lauric, oleic and linoleic.
S. Baar

1535. **Gas - liquid chromatographic determination of the fatty acid composition in oil from seeds of *Ulmus*.** I. Sørensen and P. Søltoft (Danmarks Tek. Højskole, Copenhagen, Denmark). *Acta Chem. Scand.*, 1958, **12** (5), 814–822 (in English).—Convert the fatty acids into their methyl esters. Separate the C_8, C_{10} and C_{12} methyl esters by low-pressure chromatography at 180° on a column of

silicone grease on either sodium chloride or stainless-steel Dixon rings as stationary phase, with N as carrier gas. Separate the C_{14}, C_{16} and C_{18} esters by chromatography at 200°. The results may be accurate within $\simeq 5\%$ for the lower acids and within $\simeq 10\%$ for the C_{18} acids. A. R. ROGERS

1536. **Paper chromatography of antioxidants.** R. ter Heide (N. V. Chemische Fabriek "Naarden," Naarden, The Netherlands). *Fette, Seif., Anstrichmitt.*, 1958, **60** (5), 360–362.—A paper-chromatographic method is described for the detection of alkyl gallates ($<0{\cdot}001\%$), butylated hydroxyanisole (BHA) ($<0{\cdot}005\%$) and butylated hydroxytoluene (BHT) ($<0{\cdot}01\%$) in oils and fats. For the detection of gallates and BHA, a weighed sample (40 g) of fat in 250 ml of light petroleum (boiling-range 40° to 60°) is extracted with 1 × 40 ml and 1 × 20 ml of methanol. Water (20 ml) is added to the combined methanol extracts, the light petroleum phase is discarded, and the methanol is removed by evaporation at 40° (15 mm Hg). The aq. residue is set aside for several hours at 0° and filtered. The filtrate is extracted with 20 ml of ethyl acetate. The extract is dried over Na_2SO_4, filtered and evaporated under reduced pressure to about 0·5 ml. A suitable amount of soln. is deposited on a strip of Whatman No. 1 (or S. & S. 2043b) paper which has been exposed to the mobile phase for 15 hr. The chromatogram is developed by the descending technique with light petroleum (boiling-range 95° to 110°) - benzene - acetic acid (2:2:1) as mobile phase. The 2- and 3-isomers of BHA can be separated on paper with formic acid - light petroleum (boiling-range 95° to 110°) (1:2) as solvent system, the upper phase being used to impregnate the paper and the lower as mobile phase. BHA can be separated from BHT on paper impregnated with a 75% soln. of ethyl lactate, the mobile phase comprising light petroleum (boiling-range 80° to 110°) saturated with this soln. BHT is isolated from oils by chromatography on silica gel of a *cyclo*hexane soln. E. HAYES

1537. **New spectrophotometric method for the determination of vitamin A. I. Measuring the red colour.** I. M. Jakovljevic (Lab. of the Royal Pharm. Soc., Utrecht, Netherlands). *Pharm. Weekbl.*, 1958, **93** (12), 585–593 (in English).—The method is based on the formation of the red colour which develops, after a transient blue, when a soln. of tungstophosphoric acid is added to a $CHCl_3$ soln. of vitamin A in the presence of acetic anhydride. Concentrates containing over 50,000 i.u. per g may be assayed without saponification. When saponification is necessary, Mulder's method, which dispenses with the extraction with ether, is recommended (see below). Standard curves were prepared by applying the method to cryst. vitamin-A acetate and vitamin-A alcohol (obtained by saponifying the acetate), respectively. For vitamin-A preparations containing <3000 i.u. per g, dissolve the sample in $CHCl_3$ mixture (containing exactly 1% of abs. ethanol), make up an aliquot containing 50 to 300 i.u. to 15 ml, add acetic anhydride (2 ml) and exactly 0·15 ml of tungstophosphoric acid soln. [0·3 g in a mixture of ethyl acetate (10 ml) and water (0·15 ml)]. Keep at 50° for 15 min., cool to room temp., keep for 30 min. in darkness, dilute to 25 ml with $CHCl_3$ mixture, and allow to stand for a further 30 min. in darkness. Measure the extinction in 2-cm cells at 538 to 540 mμ against a $CHCl_3$ blank. The red colour developed is stable for 1 hr. In an alternative procedure for preparations containing any concn. of vitamin A, 0·04 ml of the tungstophosphoric acid soln. is used instead of 0·15 ml. The method is rapid and the results agree well with those obtained by u.v. spectrophotometry. In Mulder's method of saponification the sample (50 to 250 mg) is heated for 20 min. under reflux with *N* alcoholic KOH (10 ml). Benzene (25 ml) is added to the cooled soln. and the alcoholic phase is removed by washing successively with *N* aq. KOH (10 ml), 0·5 *N* aq. KOH (10 ml), water (5 × 10 ml), and 0·5 *N* aq. KOH. The benzene soln. of vitamin A is dried with anhyd. Na_2SO_4 (1 g), then a 10-ml aliquot is evaporated in a stream of CO_2 at a temp. not exceeding 40°, and the residue is made up to 15 ml with $CHCl_3$ mixture before proceeding as described above. A complete evaporation is not essential as benzene does not interfere, nor do the usual antioxidants, nor vitamin D; ethanol, light petroleum and *cyclo*hexane must be removed completely. Preparations containing surface-active materials must be saponified before determination. A. TESSLER

1538. **Determination of vitamin D by a chemical method involving chromatography and colour inhibition.** J. B. Wilkie, S. W. Jones and O. L. Kline (Div. of Nutrition, Food and Drug Admin., Washington, D.C.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1958, **47** (6), 385–394.—A method is described in detail for the determination of vitamin D (**I**) in pharmaceutical products. The sample should contain 1000 to 2000 i.u. of **I** and $>20{,}000$ i.u. of vitamin A (**II**). If the sample does not contain **II**, add about 3000 i.u. of **II** before the analysis; if the sample does not contain an antioxidant, add fresh cottonseed oil (1 ml). The method involves saponification, extraction of the unsaponifiable matter, separation of **I** from **II** and other extraneous substances by chromatography on standardised MgO, separation of **I** from degradation products of **II** by chromatography on standardised Al_2O_3 and absorptiometry at 500 mμ after reaction with $SbCl_3$ - acetyl chloride - 1:2-dichloroethane reagent. The specificity of the reaction is improved by use of a correction based on the extinction at 550 mμ, a reaction blank in the presence of acetic anhydride, which completely and selectively inhibits the **I** - $SbCl_3$ reaction, and an internal standard of **I**. The results of independent determinations indicate a reproducibility of $\simeq \pm 2\%$ for syrups and elixirs and of $\simeq \pm 10\%$ for capsules. A. R. ROGERS

1539. **Photonephelometric determination of vitamin B_1 (thiamine).** V. N. Bernshtein (Pyatigorsk Pharm. Inst.). *Zhur. Anal. Khim.*, 1958, **13** (3), 365–366.—The photonephelometric determination of thiamine in preparations and medicinal mixtures is based on the pptn. of thiamine with sodium tungstophosphate. W. ROUBO

1540. **The fluorimetric determination of vitamin B_2 in native products in the presence of other vitamins.** M. Bercovici. *Rev. Chim., Bucharest*, 1958, **9** (6), 335–336.—The method is based on the fact that thiochrome formed from thiamine does not fluoresce in neutral or acid soln., while riboflavine does and can therefore be determined. H. SHER

1541. **Microbiological determination of nicotinic acid in Indian foodstuffs.** P. N. Sen Gupta (Dept. of Anthropol., Gov. of India, Indian Museum, Calcutta). *Indian J. Appl. Chem.*, 1958, **21** (1),

45–54.—Nicotinic acid was determined microbiologically by the use of *Lactobacillus arabinosus* 17–5 and *Leuconostoc mesenteroides* on 10 Indian foodstuffs, prepared by hydrolysis with acid, alkali, or Taka-diastase plus papain. The best results were obtained by using *Lb. arabinosus* and hydrolysis with *N* H_2SO_4 at 15 lb pressure for 15 min. Recovery experiments with added nicotinic acid confirmed the preliminary results. *Ln. mesenteroides* apparently does not utilise all the derivatives of nicotinic acid as completely as does *Lb. arabinosus*. The technique developed was applied to a large number of Indian foodstuffs and alcoholic beverages obtained from different areas; the results were in all cases higher than those obtained by colorimetric methods. M. D. ANDERSON

1542. **Volumetric determination of ascorbic acid with Variamine blue as indicator.** L. Erdey and L. Káplár (Inst. für Allgemeine Chemie der Tech. Univ., Budapest, Hungary). *Z. anal. Chem.*, 1958, **162** (3), 180–187.—Procedures are described and results given for the determination of ascorbic acid in dil. acetic acid soln. and in extracts of tablets and plants by titration with 0·1 *N* or 0·01 *N* soln. of chloramine T, iodine, KIO_3, $KH(IO_3)_2$, $(NH_4)_2SO_4.Fe_2(SO_4)_3$ or $FeCl_3$, with Variamine blue as indicator. The error is $\simeq \pm 0{\cdot}1\%$. A. R. ROGERS

1543. **Development of the potentiometric determination of vitamin C.** K. Kohla (Bundeslehr- und Versuchsanstalt, Pizelstätten, Kärnten, Austria). *Öst. ChemZtg*, 1958, **59** (11–12), 151–154.—The method enables ascorbic acid and dehydroascorbic acid to be determined simultaneously in the presence of other substances, which usually interfere with colour indicator titrations. The soln. containing ascorbic acid (10 ml, 0·002 g) is treated with 3% acetic acid (1 ml) and KI soln. (4%) (2·5 ml). The soln. is then titrated potentiometrically with N-bromosuccinimide (0·01%), with calomel and platinum electrodes. Two titrations are required. The first when ascorbic acid and other substances are titrated together and a second, carried out after the destruction of ascorbic acid with ascorbinase. Dehydroascorbic acid is identified by a separate inflection on the titration curve. The method is applicable to the determination of ascorbic acid and dehydroascorbic acid in vegetables, meat products, milk and urine. No previous isolation of vitamin C from these products is required. E. DUX

1544. **Modified indophenol - xylene extraction method for the determination of ascorbic acid in soya-beans.** F. B. Weakley and L. L. McKinney (U.S. Dept. of Agric., Peoria, Ill., U.S.A.). *J. Amer. Oil Chem. Soc.*, 1958, **35** (6), 281–284.—Elimination of the interference caused by mercapto groups in the indophenol - xylene method of determining ascorbic acid in germinating soya-beans is proposed. This modification of the standard method ("Methods of vitamin assay," 1951, 2nd Ed., Ass. of Vitamin Chemists Inc., Interscience Publishers, Inc., New York, pp. 71–106) requires that to determine the total dye-decolorising substances, buffer soln. is added to an aliquot of the extract, followed by the addition of 2·5 ml of a 0·005 *M* *p*-chloromercuribenzoic acid soln., employed as the more sol. alkali salt; the residual dye is then extracted in the normal manner. Determinations with the modified method on 4-day-germinated seeds gave results 15 to 54% lower than those with the standard procedure. The presence of ascorbic acid and mercapto groups in acidified extracts has been demonstrated by paper chromatography with *n*-butanol - 2% oxalic acid (2:3). G. R. WHALLEY

1545. **Paper-chromatographic behaviour of some products of decomposition of vitamin C.** W. Feldheim and M. Czerny (Inst. für Ernährung in Potsdam-Rehbrücke, Dtsch. Akad. der Wissenschaften zu Berlin). *Z. anal. Chem.*, 1958, **162** (3), 193–197.—The following approx. R_F values were found by paper chromatography with *n*-butanol - acetic acid - H_2O (4:1:5) as solvent: L-ascorbic acid, 0·37; 2:3-dioxo-L-gulonic acid, 0·12; Ca 2:3-dioxo-L-gulonate, 0·38; L-threonic acid, 0·38; 2-oxo-L-gulonic acid, 0·15; lithium, sodium, potassium or ammonium 2-oxo-L-gulonate, 0·11. A. R. ROGERS

See also abstracts—**1354**, Determination of ethanol in wine. **1428**, Determination of iodine in milk. **1487**, Determination of amylase in cereals. **1512**, Determination of components of vitamin-B complex.

Sanitation

Analysis of air, water, sewage, industrial wastes, industrial poisons.

1546. **The spectrographic determination of beryllium in air by the rotating disc technique.** U.K.A.E.A. Industrial Group, Chem. Services Dept. (Operations Branch, Springfields, Lancs.). U.K.A.E.A. Report IGO-AM/S-127, 1958, 17 pp.—The air to be analysed is drawn through a filter-paper which is then wet-oxidised with H_2SO_4 and HNO_3. Scandium is added to the resulting soln. as internal standard and it is then spectrographed by the rotating disc technique, a medium quartz spectrograph being used. The method is applicable to quantities of beryllium in the range 0·03 to 50 μg and has coeff. of variation of $\pm 20\%$ at the 0·03-μg, $\pm 14\%$ at the 1-μg and $\pm 8\%$ at the 20-μg levels. W. T. CARTER

1547. **Polarographic determination, with solid electrodes, of ozone and chlorine in the air of industrial buildings.** I. B. Kogan (Ukrain. Sci. Res. Inst. Occup. Hygiene and Diseases). *Zhur. Anal. Khim.*, 1958, **13** (2), 225–228.—A method for determining low concentrations of ozone in air and of chlorine in air and liquid has been described. In both cases iodide ion is oxidised to iodine; thus—

$$O_3 + 2I^- + H_2O \rightarrow I_2 + O_2 + 2OH^-$$
$$Cl_2 + 2I^- \rightarrow I_2 + 2Cl^-.$$

The iodide ion which has not reacted is oxidised polarographically; a solid platinum anode is used. In both cases 0·1 *M* HCl is used as supporting electrolyte or 0·1 *M* $MgCl_2.6H_2O$ soln. can be used for Cl. The $E_{\frac{1}{2}}$ is + 0·55 V. W. ROUBO

1548. **Photometric determination of micro amounts of copper in water, soils and biological materials with nickel diethyl phosphorodithioate.** A. I. Busev and M. I. Ivanyutin. *Vestn. Moskov. Univ.*, 1958, (2), 177–181.—Soln. of cupric diethyl phosphorodithioate in organic solvents are stable and of intense yellow - orange colour. To determine Cu in water, place 1 or 2 litres in a separating funnel and add 10 or 20 ml of 6 *N* copper-free H_2SO_4, 5 or 10 ml of CCl_4 and 1 or 2 ml of aq. 0·005 *M* nickel diethyl phosphorodithioate. Shake the mixture for

5 min. to extract the copper salt, repeat the extraction, combine the extracts, filter through a dry filter-paper into a 25-ml flask, make up to vol. with CCl_4 and measure the extinction on a Duboscq colorimeter. Prepare standard soln. similarly, with a soln. of $CuSO_4.5H_2O$ containing 0·02 mg of Cu per ml. It is shown that this method can detect 0·01 μg of Cu at a limiting dilution of 1 in 1×10^9. To determine Cu in soils, ignite 3 to 5 g of the powdered air-dry soil in a porcelain crucible in a muffle-furnace at 550°, cool the residue, transfer it to a beaker, and heat it with 20 to 30 ml of aqua regia on a water bath until almost dry (3 to 4 hr.). Add 20 or 30 ml of water and filter through a medium filter-paper into a 100- or 200-ml flask, washing with 0·1 or 0·2 *N* HNO_3, and make up to the mark. Determine Cu in the soln., as described above, on a 100- or 200-ml aliquot. To determine Cu in vegetable or animal matter, ash 5 to 10 g of the material, dried to const. wt., in a porcelain dish, first over an open flame and finally in a muffle-furnace at 500°. The ignition may be accelerated by the addition of a few drops of conc. HNO_3. Treat the resulting white ash with 5 or 10 ml of dil. HNO_3, dilute with water and filter into a 100- or 200-ml flask; use this soln. for the determination.

C. D. KOPKIN

1549. **The determination of chlorides in water using mercuric thiocyanate.** H. Ambühl (Chem. Lab., Kanton Aargau, Switz.). *Mitt. Lebensmitt. Hyg., Bern*, 1958, **49** (4), 241–246.—An acid soln. containing Cl^- treated with mercuric thiocyanate causes the formation of mercuric chloride and free SCN^-, which react with Fe^{3+} to give a coloured product with an extinction maximum at 490 mμ. The calibration curve is non-linear. No interference was caused by NH_4^+, PO_4^{3-}, SO_4^{2-}, Fe (<0·02 mg per litre), NO_2^- and alkaline earths.

S. BAAR

1550. **An indirect permanganate method for the determination of nitrates in water.** D. Ceauşescu and F. Pirvu (Inst. of Hygiene, Timişoara, Romania). *Rev. Chim., Bucharest*, 1958, **9** (6), 305–307.—*Procedure*—A 5-ml sample of water, diluted so that less than 10 ml of 0·0004 *M* $KMnO_4$ is required, is treated with 0·4 ml of 13·5% NaCl, exactly 5 ml of 0·001 *M* indigo carmine, and gradually with 10 ml of conc. H_2SO_4, agitating continuously. After 2 min., 40 ml of H_2O is added and the soln. is titrated a drop at a time with 0·0004 *M* $KMnO_4$ to a clear yellow colour. A correction is made for reducing substances present of 0·15 to 0·3 ml of $KMnO_4$ for oxidation values of 5 mg to 10 mg of $KMnO_4$ per litre. The results are compared with those when standard soln. of KNO_3 are titrated under similar conditions. The error is claimed to be >0·1 to 0·2 ml of 0·0004 *M* $KMnO_4$.

H. SHER

1551. **Rapid determination of nitrates in fresh water.** Me-Keng Hsu, Ken-Fang Wen and Yung-Feng Jen (Inst. of Hydrobiology, Acad. Sinica). *Acta Chim. Sinica*, 1958, **24** (4), 329–332.—The method of Nelson *et al.* (*Anal. Abstr.*, 1954, **1**, 2386) has been modified and is applied to the determination of nitrates in fresh water. The sensitivity and reproducibility of the test are improved by adding a trace of $CuSO_4$ and the removal of nitrite is effected by the use of NaN_3. *Procedure*—To the water sample (8 ml) in a 15-ml centrifuge tube add acetic acid reagent (2 ml) containing 16·3 μg of Cu^{2+} as $CuSO_4.5H_2O$ and 0·26 mg of NaN_3. Mix well, allow to stand for 10 min., then immerse the tube in a boiling-water bath for 3 min. Cool and add 0·6 g of a powdered mixture of $BaSO_4$ (100 g), $MnSO_4.H_2O$ (10 g), zinc powder (2 g), citric acid (75 g), sulphanilic acid (1 g) and 1-naphthylamine (2 g). Stopper the tube, shake, then centrifuge for 10 min. Measure the extinction of the supernatant liquid at 515 mμ. The proposed method is rapid and sensitive to 0·02 p.p.m. of nitrate. The recovery of added nitrate N is within 5% of theoretical.

S. H. YUEN

1552. **Studies on voltammetric analysis with a rotating platinum electrode. III. Determination of dissolved oxygen.** Jinzo Hashimoto (Chem. Dept., Fac. of Sci., Tokyo Univ. of Education, Koishikawa, Tokyo). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1958, **79** (5), 583–586.—The inner electrolytic current of the cell Cd | conc. $NaNO_3$ soln. | agar bridge | sample soln. containing 0·1 *M* $NaClO_4$ | rotating platinum electrode is proportional to the concn. of O (<12 mg per litre) at pH 7 to 10. The empirical formula proposed by Armstrong (*Anal. Chem.*, 1955, **27**, 1926) holds for this cell. The sample soln. (30 ml) is mixed with *M* $NaClO_4$ (3 ml), placed in an H-type cell and its surface covered with liquid paraffin. The current is measured with a microammeter, which is calibrated with a series of standard soln., assayed by the Winkler method.

K. SAITO

1553. **Determination of artificial radioactive isotopes in water.** A. A. Bŏlinkina. *Lab. Delo*, 1958, (4), 41–44.—General details of a technique have been described to show how ^{40}K can be applied as a standard for the measurements of β-emission of dried residues obtained after the evaporation of water samples. In this way the radioactivity of artificial radioactive isotopes present in such residues can be determined. An order of sensitivity of 10^{-11} curies per litre is claimed which is less than the permissible value of radioactivity in water.

W. ROUBO

1554. **Proposed standard methods for methane determination.** American Water Works Ass. (2 Park Ave., New York). *J. Amer. Wat. Wks Ass.*, 1957, **49** (8), 1077–1084.—A Committee report is presented on a combustible gas indicator method and the Orsat method. (7 references.)

G. HELMS

1555. **Determination of traces of salts in purified boiler-feed water.** S. Zagrodzki and H. Zaorska (Lodz, Poland). *Chem. Tech., Berlin*, 1958, **10** (4), 210–212.—The apparatus described includes a spectrophotometer, and concn. down to 2×10^{-7} *N* (for K^+) can be measured. Results are automatically recorded, and the apparatus can control the water intake when salt concn. becomes excessive. The use of the apparatus in the sugar industry is discussed.

C. A. FINCH

See also Abstracts—**1217**, Determination of B in water. **1375**, Determination of phenols in wastes.

Agricultural analysis

Soil, fertilisers, herbicides, pesticides, animal feeding-stuffs.

1556. **Influence of alcohol on the flame-spectrometric determination of plant-available magnesium in soils.** P. Schachtschabel and U. Schwertmann (Hannover-Herrenhausen). *Z. PflErnähr. Düng.*,

1958, **82**, 38–42.—Available Mg in soil is extracted (2 hr.) with 0·025 *N* $CaCl_2$ containing 10% of *iso*-propyl alcohol. The alcohol serves to increase the emission at 371 mμ, widen the useful range of determination and lower the experimental error. Extracts containing Mg in the range 0 to 20 p.p.m. are used. The presence of K increases the Mg values (0·4 p.p.m. of Mg per each 10 p.p.m. of K regardless of the actual concn. of Mg) and a correction is necessary. A. G. POLLARD

1557. **Direct colorimetric determination of traces of silver in soil in the presence of other cations.** F. Popea and L. Bădiceanu. *Rev. Chim., Bucharest*, 1958, **9** (6), 323–324.—The proposed method is to treat a soln. of silver salt at pH 4 to 5 with Na acetate buffer and a soln. of EDTA (disodium salt). A dil. soln. of dithizone is added, and the silver complex is extracted with CCl_4 and the colour compared with standards. It is claimed that the method is rapid and advantageous in that reagents do not require special purification as is usual with dithizone, because the impurities are retained by the EDTA, but Cl^- must be eliminated. Silver in the presence of large amounts of Cu, Pb or Zn can be determined by this method. H. SHER

1558. **Simple colorimetric method for the determination of nitrates in forage crops.** M. P. Morris and A. González-Más (Federal Exp. Sta., Agric. Res. Service, U.S. Dept. of Agric., Mayaguez, P.R.). *J. Agric. Food Chem.*, 1958, **6** (6), 456–457.—The method described is modified from that of Swann and Adams for coating materials and nitrocellulose (*cf. Anal. Abstr.*, 1957, **4**, 871). The sample is macerated with water and filtered; 0·5 *N* NaOH and 30% H_2O_2 are added to the filtrate, which is then evaporated to dryness; conc. H_2SO_4 - $FeSO_4$ reagent is added, the colour is allowed to develop for 1 hr., and transmittance is read at 355 mμ for a faint-pink colour, or 525 mμ for medium- to dark-pink colour; the quantity of nitrate is obtained from a standard graph. The method is accurate to ±4%, and requires only 2 hr. to complete; it is suitable for following the accumulation and decline of nitrates in forage crops receiving high levels of nitrogen fertiliser. Interference by plant nitrites is negligible. The method is not applicable to a few legumes containing β-nitropropionic acid.
M. D. ANDERSON

1559. **Determination of the total phosphorus in soil with the use of perchloric acid.** H. Bohne, P. Gröpler and M. Dittmer. *Z. PflErnähr. Düng.*, 1958, **82**, 42–46.—The decomposition of the org. and inorg. phosphorus compounds in soil, as a preliminary to the determination of total P by the vanadate - molybdate method, is effected by heating the sample (1 g) with 70% $HClO_4$ (5 ml) in a covered beaker until the soil residue is white, and then for a further hour. The risk of explosion is avoided by maintaining sufficient liquid in the beaker. The method is quicker and simpler than the use of $HClO_4$ - HNO_3 mixtures.
A. G. POLLARD

1560. **Determination of organic phosphorus in soils. III. Comparison of methods.** A. Van Diest and C. A. Black (Iowa Agric. Home Econ. Exp. Sta., Ames). *Proc. Soil Sci. Soc. Amer.*, 1958, **22**, 286–287.—In five soils tested the method of Mehta *et al.* (*Ibid.*, 1954, **18**, 443) yielded consistently higher results (10 to 25%) for org. P than did that of Karla and Virtanen (*Maatalous. Aikakausk.*, 1955, **27**, 104). Data obtained by the two methods were not proportional. A. G. POLLARD

1561. **Phosphate determination by the molybdenum blue method using ascorbic acid as reducing agent.** E. Rauterberg and H. Ossenberg-Neuhaus (Inst. Pflanzenernähr., Tech. Univ., Berlin). *Z. PflErnähr. Düng.*, 1958, **82**, 46–49.—The method is designed primarily for determining phosphate in Ca lactate extracts of soils. To an aliquot (50 ml) of the extract is added 20 ml of 2 *N* H_2SO_4, 2·5 ml of 2% ammonium molybdate soln. and 1 ml of 0·04 *N* ascorbic acid (freshly prepared daily) and the whole is diluted to 100 ml. The flask is heated for 15 min. in a boiling-water bath and the colour intensity (stable for 24 hr.) is measured photometrically. Under these conditions SiO_2 does not interfere and amounts of P_2O_5 down to 10 μg may be determined. A. G. POLLARD

1562. **Inositol hexaphosphate. I. Determination in extracts of soils and manures.** A. G. Caldwell and C. A. Black (Iowa State Coll., Dept. Agronomy). *Proc. Soil Sci. Soc. Amer.*, 1958, **22**, 290–293.—To the air-dried soil sample (5 g) in a centrifuge tube is added HCl (20 ml) and the tube is then placed in a hot-water bath until the acid begins to boil (70°). The tube is immediately removed and a further 20 ml of HCl is added. The mixture is stirred and left at room temp. for 1 hr. and then stirred and centrifuged. The residual soil is washed with water (30 ml) centrifugally, the washings being added to the acid extract, and then dispersed in 0·5 *N* NaOH (30 ml) at room temp. for 1 hr. and centrifuged. After re-dispersion of the ppt. in 0·5 *N* NaOH, the tube is covered and placed in an oven at 90° for 8 hr. On cooling, the contents of the tube are stirred and centrifuged, the supernatant liquid being added to the previous alkaline extract. To remove interfering humus from the combined alkaline extract, HCl (20 ml) is added and, after warming to flocculate the humus, the liquid is centrifuged and the ppt. washed twice with 20 ml of hot HCl (1:10) the combined supernatant liquid and washings being then added to the original HCl extract of the soil. Inositol is separated by addition of NaOH to the final extract to produce a pH of 1·7 to 1·8 and, if necessary, an Fe-containing soln. to complete the pptn. of the Fe inositol hexaphosphate complex. The ppt. is flocculated by warming, separated by centrifuge, washed with HCl of pH 1·8, dispersed (largely dissolved) in 20 ml of HCl (0·85 *N*) and transferred (1 drop per 3 sec.) to a column of De-Acidite anion-exchange resin (60 to 80 mesh, 30 cm long), previously washed with 0·85 *N* HCl. The column is slowly eluted with HCl (0·85 *N*) at the rate of 1 drop in 3 sec. The first 500 ml of eluate is discarded, and the acid concn. increased to 1·4 *N* to yield a further 250 ml of eluate and then to 3 *N* to give a further eluate of 250 ml, the two 250-ml portions being used for the determination of inositol phosphate, after digestion with $HClO_4$, by the Dick and Bray method (*Ind. Eng. Chem., Anal. Ed.*, 1940, **12**, 665). Acid extracts of manures may be added directly to the anion-exchange column. A. G. POLLARD

1563. **Modified field test for the determination of small amounts of nickel in soils and rocks.** R. E. Stanton and J. A. Coope (Dept. of Geol., Imperial Coll., London). *Bull. Instn. Min. Metall.*, 1958, (623), 9–14.—The procedure given is a modification of the unpublished methods of Jacobson (thesis, Mass. Inst. Technol., 1954) and Kranck (thesis, London Univ., 1957). The sample (0·2 g) is fused

with $KHSO_4$ (1 g) and the melt is dissolved in *N* HCl (5 ml). To an aliquot (2 ml) of the clear soln. are added citrate buffer (5 ml) and 1 ml of furil α-dioxime soln. [0·3 g dissolved in a mixture (1 + 9, by vol.) of ethanol and benzene]. The test-tube is shaken for ≃2 min. and the yellow coloration of the Ni furil α-dioxime complex in the organic phase is compared visually with a series of nickel standards prepared similarly. From 1 to 15,000 p.p.m. of Ni can be determined to within ±25%; ≃90 samples can be analysed daily. The ratio Cu : Ni should not exceed 30; samples high in organic matter should be ignited before fusion. (*Cf. Anal. Abstr.*, 1957, **4**, 122.) W. J. BAKER

1564. **Quantitative determination of clay minerals by X-ray diffraction.** N. L. Jarvis, R. D. Dragsdorf and R. Ellis, jun. (Kansas Agric. Exp. Sta., Manhattan). *Proc. Soil Sci. Soc. Amer.*, 1957, **21**, 257–260.—The clay material mixed with MgO as internal standard is placed in a desiccator at 100% r.h. for a specified period to control the expansion of montmorillonitic lattices. The prepared sample is sealed in a glass capillary and mounted in a diffraction camera (Straumanis type). A filtered Co target tube (1·790 A) serves as X-ray source, and a microphotometer (Leeds and Northrup type) is used in recording the X-ray patterns. The integrated intensities of the 001 clay diffraction lines and the 1·48 A MgO line are determined from the density curves by plotting log density peaks in terms of intensity as a function of angle and measuring by planimeter the area under the resulting intensity peaks. The intensity constant for each mineral present may be calculated (necessary for each sample) and thence the percentage in the sample. Data for typical bentonite, illite and kaolinite are recorded. The composition of mixed clay minerals may be determined with an accuracy of ≃±3%. A. G. POLLARD

1565. **Decarboxylation of the organic matter of soils. I. Decarboxylation of total humic matter.** H. Deuel, P. Dubach and R. Bach (Agric. Inst. Tech. Hochsch., Zurich). *Z. PflErnähr. Düng.*, 1958, **81**, 189–201.—The production of CO_2 from uronic acids by treatment with 12% HCl is examined under various conditions using soil org. matter and other sources of these acids. This throws doubt on the suitability of the method of Lefèvre and Tollens (*Ber.*, 1907, **40**, 4153) for the examination of soil humus or org. manures. A. G. POLLARD

1566. **Determination of diethylstilboestrol [stilboestrol] in feed supplements by microbiological assay.** L. J. Hanka and W. R. Lockhart (Iowa State Coll., Ames, U.S.A.). *Antibiot. & Chemother.*, 1958, **8** (11), 584–589.—The method is based on the specific inhibitory effect of stilboestrol (**I**) on the growth of *Staphylococcus aureus*, strain H. Feed-supplement samples are extracted in a Soxhlet apparatus with $CHCl_3$, which is then extracted with *N* NaOH, and the **I** is re-extracted into $CHCl_3$ after acidification. Filter-paper discs carrying 0·08 ml of the test soln. are placed in contact with an agar medium seeded with the test organism. After incubation overnight at 37°, the zones of inhibition, which are proportion to the log. of the **I** concn. between about 60 and 175 μg per ml, are read. The method may be used as a 4- or 6-point assay and will detect differences of 7 to 10 μg per ml of **I** at the 5% probability level. W. H. C. SHAW

1567. **The indirect analysis of a binary mixture of polychlorinated compounds.** S. Petrascu and E. Grou (Inst. Agronom. Res., Bucharest). *Acad. R.P.R., Stud. Cercet. Chim.*, 1958, **6** (1), 127–137.—General theoretical formulae are deduced for the analysis of binary mixtures based on total chlorine, hydrolysable chlorine or both determinations. Characteristic coefficients for each chlorinated compound are used, so that numerical formulae can be applied in each case. These formulae have been verified for mixtures of hexachloro*cyclo*hexane with DDT, as well as with hexachlorobenzene. With the pure substances errors were ±0·56%, but with technical products individual errors could be as high as 14%. Empirical formulae were developed for these products which reduced the mean errors to below 0·5%. The determination of the Cl must be precise, and the method of Busch (*Ber.*, 1916, **49**, 1063) for total Cl is recommended, *i.e.*, catalytic reduction with H or hydrazine hydrate in the presence of Pd pptd. on $CaCO_3$. A modification of the usual method for hydrolysable Cl is used in that the dehydrochlorination is carried out at room temp. and not by boiling, as follows. A soln. of the substance (in 95% ethanol or benzene as required) is treated with an equal vol. of alcoholic KOH (4 *N*) for 1 hr. at ≃20°. The Cl^- are determined potentiometrically with a reference electrode of AgI and an indicating electrode of Ag. A soln. of 0·1 *N* $AgNO_3$ is titrated directly against the KCl soln. obtained from the reduction of the organic mixture after its neutralisation with 6 *N* HNO_3, with methyl orange as indicator (Böttger, "*Physikalische Methoden der analytischen Chemie*," Leipzig, 1939). H. SHER

1568. **Ion-exchange chromatography for hydrolysis products of organophosphate insecticides.** F. W. Plapp and J. E. Casida (Dept. of Entomology, Univ. of Wisconsin, Madison, U.S.A.). *Anal. Chem.*, 1958, **30** (10), 1622–1624.—Prepare a column of Dowex 1-X8 anion-exchange resin (50 g) in Cl^- form at pH >3 and apply the sample (containing ≮1 μg of phosphoric acid compounds) in aq. soln. Elute phosphoric, phosphorothioic, monoalkyl phosphoric and dialkyl phosphoric acids with aq. HCl gradients. Elute dialkyl phosphorothioic, dialkyl phosphorodithioic, monoalkyl phenylphosphoric and monoalkyl phenylphosphorothioic acids with HCl gradients in aq. methanol or aq. acetone. Analyse the separated compounds by quant. determination of total P by the method of Allen (*Biochem. J.*, 1940, **34**, 858). The purity of the eluted fractions was confirmed by ascending chromatography on Whatman No. 1 paper with *iso*propyl alcohol - aq. NH_3 as solvent; the compounds were located by the method of Hanes and Isherwood (*Nature*, 1949, **164**, 1107) or as red - brown spots on a yellow - green background by spraying with 2% $CuCl_2$ soln. and 0·5% $K_3Fe(CN)_6$ soln. A. R. ROGERS

1569. **Application of cholinesterase assay to residue analysis of 1-naphthyl methylcarbamate (Sevin).** H. H. Moorefield and E. R. Tefft. *Contr. Boyce Thompson Inst.*, 1958, **19** (4), 295–301.—The preparation is stripped with $CHCl_3$, the solvent is evaporated and the Sevin estimated enzymatically by the method of Metcalf and March (*J. Econ. Ent.*, 1949, **42**, 721). No interference was encountered from DDT, BHC, chlordane, toxaphene, dieldrin, aldrin, rotenone or pyrethrins. Phosphorus insecticides must be absent.
E. G. BRICKELL

See also Abstracts—**1516**, Determination of residual tetrachloroethylene in wheat. **1523**, Determination of allethrin residues in milk and meat.

5.—GENERAL TECHNIQUE AND APPARATUS

General

1570. **Report on recommended specifications for microchemical apparatus. Volumetric glassware. Microlitre pipettes.** Committee on Microchemical Apparatus, Div. of Anal. Chem., American Chemical Society. *Anal. Chem.*, 1958, **30** (10), 1702–1703.—Specifications for dimensions and performance are given for two patterns of microlitre pipettes; one for pipettes of 1 to 4 μl capacity and the other for pipettes ranging from 5 to 500 μl. A recommended procedure for calibration is given.
T. R. ANDREW

1571. **Mechanically-operated burettes.** J. T. Stock (Dept. of Chem., Univ. of Connecticut, Storrs, Conn., U.S.A.). *Lab. Practice*, 1958, **7** (6), 349–352.—Various mechanically-operated burettes are reviewed and a simple plunger-type electromagnetic valve, constructed from a plastic-covered magnetic stirrer-bar is described. G. SKIRROW

1572. **A rotary drier for use in the dry-ashing method for estimating protein-bound iodine.** P. Lockwood (W. Park Hosp., Epsom, Surrey, England). *J. Clin. Path.*, 1958, **11** (4), 367–368.—Rotation combined with i.r. heating gives a thin layer of dried material around the wall of the tube, simplifying incineration and leaching.
H. F. W. KIRKPATRICK

1573. **Improvements in or relating to sonic gas analysers.** Sir Howard Grubb Parsons & Co., Ltd. [Inventors: A. E. Martin and D. Mounfield]. Brit. Pat. 805,544; date appl. 6.1.56.—The analyser has means for indicating the mol. wt. of the gases or vapours under test. The time taken for sonic or ultrasonic vibrations to traverse a tube containing the gas or vapour is caused to vary the phase angle between two a.c. voltages as the mol. wt. varies, the voltages being applied to phase detection means which produce an electric current proportional to the change in the phase angle. The resulting current is passed through the actuating winding of a moving iron meter having characteristics such that a linear mol. wt. scale is obtained. J. M. JACOBS

1574. **Self-contained clepsydra-controlled fraction collector.** W. J. Wings (Dept. of Biochem., Univ. Alabama, Birmingham, U.S.A.). *Anal. Chem.*, 1958, **30** (10), 1710–1711.—The equipment described is independent of any external power supply and is a weight-driven flow-time device making use of a rotating distributor arm and indexing escapement to collect the fractions in stationary containers. The clepsydra (a timing device) incorporates intermittent siphons and a Mariotte bottle.
K. A. PROCTOR

1575. **Simple capillary viscometer.** H. E. D. Lloyd (Bland-Sutton Inst. of Path., Middx. Hosp., London). *J. Clin. Path.*, 1958, **11** (4), 363–365.—A capillary 7·5 cm long, internal diameter 0·5 mm (±0·01 mm) and external diameter about 4 mm is attached to a 1-ml Ostwald pipette by rubber pressure-tubing. The pipette is marked above and below the bulb and is water-jacketed. Values for total plasma and fibrinogen viscosity relative to H_2O in 45 healthy subjects are recorded.
H. F. W. KIRKPATRICK

1576. **A new addition apparatus.** I. Scheer and A. F. D'Adamo, jun. (Ortho Research Foundation, Raritan, New Jersey). *J. Chem. Educ.*, 1958, **35** (6), 281.—The apparatus described is designed for the controlled addition to a reaction mixture of solid reagents that are sensitive to air and moisture, *e.g.*, $AlLiH_4$ or NaH. O. M. WHITTON

Chromatography, ion exchange, electrophoresis

1577. **Improved grid for the determination of R_F values in paper chromatography.** I. F. Bird (Res. Inst. for Plant Physiology, Imp. Coll., London). *Lab. Practice*, 1958, **7** (6), 359–361.—The grid is constructed from Perspex sheet marked with grooves in such a way that, when positioned correctly on the base line and solvent front, the R_F value of a spot may be read off directly from its position under the grid. G. SKIRROW

1578. **Chromatography by radial development.** L. Peyron (Lab. de Recherches, Éts. A. Chiris, Grasse, France). *Bull. Soc. Chim. France*, 1958, (6), 889–899.—A review of methods and applications. (302 references.) E. J. H. BIRCH

1579. **Automatic recording of extinction coefficients of successive eluate fractions from column chromatograms.** F. Turba and N. Heimburger (Inst. of Physiol. Chem., Univ. of Munich). *Biochem. Z.*, 1958, **330** (5), 359–364.—An apparatus is described which automatically samples eluate fractions from column chromatograms, and records the extinction coefficient or optical density of each fraction. This apparatus, which is simple and rapid in action, is especially applicable to sensitive compounds, and also to methods in which other treatments of the fractions are desired. The principal use is in protein and peptide chromatographic separations, but it can be used in other separation procedures, *e.g.*, column electrophoresis and counter-current distributions. D. B. PALMER

1580. **Zone electrophoresis on filter-paper: a simple modification to the horizontal type of apparatus to reduce handling of the strips.** R. A. Brenan (Ludgater Lab., Gen. Hosp., Burton-on-Trent). *Clin. Chim. Acta*, 1958, **3** (5), 499–500.—Weights made from glass rod are attached to each end of the strip to keep the paper taut. The strip is supported on a frame, also made from glass rod, which can be removed and placed in an oven for drying after electrophoresis. H. F. W. KIRKPATRICK

1581. **Mechanical coulometer for the electrophoresis of proteins.** G. B. Kobozev. *Ukr. Biokhim. Zhur.*, 1957, **29** (3), 375–380; *Ref. Zhur., Khim., Biol. Khim.*, 1958, Abstr. No. 11,890.—In order to increase the accuracy of measurement of mobility by free electrophoresis it is proposed to measure the quantity of electricity flowing through the dish during the experiment rather than measure the strength of the current; this eradicates errors due to changes in conductivity of the solution arising from the effects of heat, diffusion, etc. A mechanical coulometer was constructed, which worked with stability at I = 0·1 A and over. It embodies its own constant-current commutator, combined with a revolution counter, the reading on which is proportional to the number of coulombs passing through the motor and dish during the experiment. A diagram is given and the method of calibration is described. The use of the coulometer need not be

restricted to the measurement of mobility by electrophoresis as it can be used for the measurement of small amounts of electricity in other experiments.
K. R. C.

See also Abstracts—**1184**, Presentation of gas-liquid chromatographic data. **1185**, Terms and units in gas chromatography. **1186**, Units of measurement in gas chromatography.

Optical

1582. **General qualitative and semi-quantitative emission spectrographic system.** T. M. Holager (Forsvarets Forskningsinst., Avd. for Kjemi, Kjeller pr Lillestrøm, Norway). *Tidsskr. Kjemi. Bergv.*, 1957, **17** (4), 58–62.—The system which covers 70 elements, is based upon a master plate (dimension 25 cm × 5 cm) file, a two-plate comparator, a grating spectrograph (dispersion 5 A per mm, 1st order), and semi-quantitative visual calibration curves. The wavelength range used is 2300 A to 3550 A (2nd order) and 3550 A to 8550 A (1st order). The plate file consists of six several-element master plates (20, 31, 42, 18, 15 and 8 elements in the six wavelength regions) and of 134 single-element plates. The mixtures of elements, mostly as oxides, are charged into carbon electrodes ("National" special) in quantities inversely proportional to the sensitivities of the most persistent lines and mixed with carbon powder. The samples are arc-excited (anodic) and a step sector is used. Every plate has also spectra of carbon and of iron. The single-element plates are prepared in the same manner, 2 mg to 3 mg of the element in question being used. For qualitative analysis five sensitive lines (wavelengths are given) for every element are marked on the master plates and also tabulated on special sheets for easy reference. For quantitative analysis one analysis line and two reference lines are marked on the master plates. The internal standards used are Cr_2O_3 - La_2O_3, Li_2CO_3 - Bi_2O_3, and CdO - Sb_2O_4 in the wavelength ranges 2300 A to 3550 A, 3550 A to 6050 A, and 6050 A to 8550 A. Two internal standards are used, different in different regions, one element being held as a reserve if the other element should happen to be present in the sample. The proportion of sample to internal standard to carbon used is 90:5:100. The concn. range covered is 0·01 to 1%. Calibration curves are plotted on semi-logarithmic paper: difference between number of visual steps for analysis and reference lines (accuracy ± 0·25 step) against percentage sample composition. The accuracy of the method is generally ±25% (relative). The system has proved efficient for analytical work.
B. Rönnholm

1583. **Ultra-micro flame spectrophotometer.** D. Exley and D. Sproat (Dept. of Biochem., Oxford). *J. Sci. Instrum.*, 1958, **35** (6), 202–206.—An integrating circuit and electronic switching arrangement incorporated in a Beckman DU flame spectrophotometer increases the sensitivity 1000-fold. Burning the samples dissolved in acetone increases the sensitivity 60,000-fold, enabling 3×10^{-13} g of Na and 10^{-10} g of Mg to be detected.
G. Skirrow

1584. **Efficient continuous a.c. arc.** J. T. Rozsa and O. W. Uguccini (Nat. Spectrographic Lab., Inc., Cleveland, Ohio). *Appl. Spectroscopy*, 1958, **12** (2), 33–35.—An electrically efficient and improved version of the high-voltage a.c.arc is described which shows the characteristic advantage over the d.c. arc in improved spectrographic reproducibility. The greatest improvement is effected in the determination of heavy or refractory elements, and a table of typical accuracies and sensitivities is shown.
P. T. Beale

1585. **Design for a multi-channel infra-red spectrometer using transistor electronics.** D. G. Avery and R. C. Bowes (Royal Radar Estab., Great Malvern, Worcs., England). *J. Sci. Instrum.*, 1958, **35** (6), 212–216.—Details are given of a spectrometer in which a number of indium antimonide photocells are placed in the plane of the spectrum, each acting as its own exit slit and receiving light of different wavelengths. The circuitry permits their output to be handled separately or coupled to record intensity differences at two wavelengths.
G. Skirrow

1586. **Potassium bromide disc technique for infra-red micro-analysis with freeze-drying of samples soluble in organic solvents but insoluble in water.** H. P. Schwarz, R. C. Childs, L. Dreisbach, S. V. Mastrangelo and A. Kleschick (Philadelphia General Hosp., Pa., U.S.A.). *Appl. Spectroscopy*, 1958, **12** (2), 35–38.—A technique for the preparation of potassium bromide discs by freeze-drying before pressing is applicable in cases when organic solvents are essential for dissolving the sample but are unsuitable for spectroscopic determinations in liquid cells. Important features are the avoidance of contamination during sample preparation and the lubrication of the die with graphite. Measurements on 76 discs prepared from 38 samples of 3 different compounds showed an over-all standard error of ±0·5% and reproducible results were obtained on binary mixtures.
P. T. Beale

1587. **Performance of the Beckman DK spectrophotometer.** L. Cahn and B. D. Henderson (Cahn Instrument Co., Paramount, Calif.). *J. Opt. Soc. Amer.*, 1958, **48** (6), 380–387.—A comprehensive set of tests has been developed for assessing the performance of Beckman DK-1 and -2 spectrophotometers. The 20 tests comprise—time stability of the 100% reading at a single wavelength over a period of several hours; constancy of the 100% reading over three selected wavelength ranges (u.v., visible and i.r.); stray radiation (u.v. and i.r.); resolution (u.v., visible and i.r.); photometric accuracy; reproducibility; slit width and noise tests (u.v., visible and i.r.); zero stability (u.v., visible and i.r.); flashlight test (for light leaks); electrical interference test; and range switching test. The tests can be modified to suit other types of photo-electric recording spectrophotometer.
B. S. Cooper

1588. **Adaptation of the Beckman model B spectrophotometer to the measurement of dilute fluorescent solutions.** L. P. Joly, G. Sabolewski and G. Nadeau (Hosp. Saint-Michel Archange, Quebec, Canada). *Clin. Chem.*, 1958, **4** (4), 286–289.—A fluorimetric attachment that entails no major modifications of the instrument is described.
H. F. W. Kirkpatrick

1589. **Small infra-red spectrometer.** J. U. White, N. L. Alpert and S. Weiner (The White Development Corp., Stamford, Conn., U.S.A.). *Rev. Sci. Instrum.*, 1958, **29** (6), 511–516.—Design and constructional details are given. The instrument has a rock-salt prism (40 × 50 mm base) and records the spectra

of samples linearly in transmittance or absorbance as a function of wavelength on flat 8 × 23·5 in. charts. It will scan 2 to 16 microns in 16 min. with a resolution of 3 to 4 cm^{-1} at 10 microns and scattered light of <1% at 15 microns. Accessories include holders for gas absorption cells, liquid cells (these latter being convertible to variable space cells) and a special holder for solid samples, which takes mull, films or pressed pellets. G. SKIRROW

1590. **Micro-sampling for small infra-red spectrophotometers.** J. U. White, S. Weiner, N. L. Alpert and W. M. Ward (The White Development Corp., Stamford, Conn., U.S.A.). *Anal. Chem.*, 1958, **30** (10), 1694–1698.—A 3-lens beam condenser has been built to fit into the sample space of the Beckman infra-red spectrophotometers. This enables 75% of the light to pass through a 0·5 mm × 4 mm sample area by forming a 5-fold reduced image of the slit and then re-magnifies it. Small capillary absorption cells of this size have been used to record the spectra of several essential-oil samples. Potassium bromide discs (1 mm × 5 mm) have been pressed for solid samples. K. A. PROCTOR

1591. **Circulation-type apparatus for spectrophotometric titrations.** T. R. Sweet and J. Zehner (Ohio State Univ., Columbus 10, U.S.A.). *Anal. Chem.*, 1958, **30** (10), 1713.—The apparatus described can be used with the Beckman DU spectrophotometer. In the simultaneous determination of Cu and Fe, the coeff. of variation was 2·6% for Cu and 1·9% for Fe, based on the results of 8 observations. K. A. PROCTOR

1592. **Emission micro-X-ray spectrography of metals.** G. A. Gumanskii. *Izv. Akad. Nauk UzSSR, Ser. Fiz.-Matem. N.*, 1957, (3), 27–37; *Ref. Zhur., Khim.*, 1958, Abstr. No. 46,432.—The processes of formation of emission X-ray spectra, the method of obtaining which and the analysis of which have been previously described (Gumanskii, *Hutn. Listy*, 1952, **6**, 303), are studied. It is established that the emission from samples of large thickness is not a simple function of the atomic number of the radiating element, which contradicts the data of Shearer (*Phil. Mag.*, 1922, **44**, 793) and supports the work of Vette and Holthusen (Vette, *Ann. Phys.*, 1930, **5**, 8, 929; Holthusen, *Acta Radiol.*, 1927, **8**, 51). The photo-electronic emission has two components: fast (with energy >30 keV) but formed of Compton electrons and primary photo-electrons, and slow (with energy <30 keV), formed of Compton electrons and secondary and primary electrons (for atomic numbers from 30 to 50). These components have differing dependence on the atomic number of the emitting element and on the effective wavelength of the exciting radiation. The slow electrons are the main factor ensuring resolution of the elements on the micro-X-ray spectra. With a correctly chosen set of conditions for the photography, photometric analysis of the emission micro-X-ray spectra ensures the resolution of elements with a difference of atomic numbers of ≤4.
C. D. KOPKIN

1593. **Remotely operated filter photometer.** M. T. Kelley, E. B. Wagner, W. L. Maddox, H. C. Jones and D. J. Fisher (Oak Ridge National Lab., Tenn., U.S.A.). *Anal. Chem.*, 1958, **30** (10), 1711–1712.—The instrument described was designed for master slave manipulation, and the relative standard deviation of routine remote colorimeter analyses is about 5%. K. A. PROCTOR

Thermal

1594. **The standardisation of the techniques of differential thermal analysis.** G. Gita. *Rev. Chim., Bucharest*, 1958, **9** (6), 313–316.—It is stated that the results of such analyses depend on apparatus, the method of procedure adopted, and the samples used for standardisation. The shape and size of the furnace, its thermal inertia and calorific asymmetry affect the results. The nature and size of the thermocouple, as well as the method of recording, the speed of chart movement and the dimensions of the abscissae, all produce variations in the shape of the thermal diagram. The compactness of the sample, the size of the individual particles, as well as the moisture content and crystalline state, are other varying factors. Recommendations are made for standardising methods of preparation of materials for standardising equipment. H. SHER

Electrical

1595. **Voltammetric studies with the graphite indicating electrode.** P. J. Elving and A. F. Krivis (Dept. of Chem., Univ. of Michigan, Ann Arbor, U.S.A.). *Anal. Chem.*, 1958, **30** (10), 1645–1648.—The graphite electrode described, impregnated with ceresin wax, has been studied under standard conditions in both organic and inorganic systems. In mineral acid soln. penetration of the wax coating results in poor reproducibility. Satisfactory results were obtained in slightly acid and neutral media. Alkaline media were not investigated. Experimental conditions must be carefully controlled for good results. K. A. PROCTOR

1596. **Anodic chronopotentiometry with a graphite electrode. Analytical applications.** P. J. Elving and A. F. Krivis (Dept. of Chem., Univ. of Michigan, Ann Arbor, U.S.A.). *Anal. Chem.*, 1958, **30** (10), 1648–1652.—Investigations into the use of electrolysis at constant current with a graphite electrode showed that, whilst organic reductions gave poor results, better results were obtained with organic oxidations. Dihydroxybenzene and phenylenediamine isomers have been studied individually and in mixtures over a wide pH range.
K. A. PROCTOR

1597. **Graphical method for the determination of the inflection point of a symmetrical potentiometric titration curve.** R. Kohn and V. Zítko (Dept. of Carbohydrates and Biochem., Chem. Inst., Acad., Sci., Bratislava, Czechoslovakia). *Chem. Zvesti*, 1958, **12** (5), 261–274.—The method is based on the comparison of the areas bounded by the titration curve and a straight line which cuts through it in three points. If the straight line passes through the inflection point, the areas cut off are equal; this has been confirmed mathematically. For comparison of the size of the areas, visual evaluation is sufficient. The results of the determination of the inflection point obtained with the use of the described method by neutralisation, pptn. and redox titration have been compared with those obtained by other graphical methods. J. ZÝKA

ABBREVIATIONS

Certain abbreviations in everyday use are not included in the following list. When any doubt might arise from the use of an abbreviation or symbol the word is printed in full.

alternating current	a.c.
ampere	amp.
Ångström unit	Å
anhydrous	anhyd.
approximate, -ly	approx.
aqueous	aq.
atmospher-e, -ic.	atm.
boiling-point	b.p.
British thermal unit	B.Th.U.
calorie (large)	kg-cal.
calorie (small)	g-cal.
centimetre	cm
coefficient	coeff.
concentrated	conc.
concentration	concn.
constant	const.
corrected	(corr.)
crystalline / crystallised	cryst.
cubic	cu.
current density	c.d.
cycles per second	c/s
density	ρ
density, relative	d or wt. per ml
dilute	dil.
direct current	d.c.
distilled	dist.
ethylenediaminetetra-acetic acid	EDTA
electromotive force	e.m.f.
equivalent	equiv.
gram	g
gram-molecule	mole
half-wave potential	$E_{\frac{1}{2}}$
hour	hr.
hydrogen ion exponent	pH
infra-red	i.r.
insoluble	insol.
international unit	i.u.
kilogram	kg
kilovolt	kV
kilowatt	kW
liquid	liq.
maxim-um, -a	max.
melting-point	m.p.
microgram	μg (not γ)
microlitre	μl
micromole	μmole
micron	μ
milliampere	mA
milli-equivalent	milli-equiv.
milligram	mg
millilitre	ml
millimetre	mm
millimicrogram	mμg
millimolar	mM
millivolt	mV
minute (time)	min.
molar (concentration)	M
molecul-e, -ar	mol.
normal (concentration)	N
optical rotation	α_λ^t
ounce	oz
parts per million	p.p.m.
per cent.	%
per cent. (vol. in vol.)	% (v/v)
per cent. (wt. in vol.)	% (w/v)
per cent. (wt. in wt.)	% (w/w)
potential difference	p.d.
precipitate (as a noun)	ppt.
precipitated	pptd.
precipitating	pptg.
precipitation	pptn.
preparation	prep.
qualitative, -ly	qual.
quantitative, -ly	quant.
recrystallised	recryst.
refractive index	n_λ^t
relative band speed	R_F
relative humidity	r.h
revolutions per minute	r.p.m.
saponification value	sap. val.
saturated calomel electrode	S.C.E.
second (time)	sec.
soluble	sol.
solution	soln.
specific gravity	sp. gr.
specific rotation	$[\alpha]_\lambda^t$
square centimetre	sq. cm
standard temp. and pressure	s.t.p.
temperature	temp.
ultra-violet	u.v.
vapour density	v.d.
vapour pressure	v.p.
volt	V
volume	vol.
watt	W
wavelength	λ
weight	wt.

In addition, the following symbols may be used in conjunction with numerical values or in mathematical expressions—

greater than	$>$	less than	$<$
not greater than	$\ngtr$	not less than	$\nless$
is proportional to	$\propto$	of the order of, approximately	$\simeq$

The principal Pharmacopoeias are denoted by B.P., U.S.P. or D.A.B., together with the identifying roman numeral or year.

Valency states are represented by a superscript roman numeral, *e.g.*, Fe^{II}, Mo^{V}. Substances in the ionic state are represented by Na^+, Fe^{3+}, Fe^{3+}, etc., for cations and by Cl^-, SO_4^{2-}, PO_4^{3-}, etc., for anions.

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